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EXPERIMENTAL CHEMISTRY.

PART I.

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EXPERIMENTAL CHEMISTRY

FOR

JUNIOR STUDENTS.

BY

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PART I.—INTRODUCTION.

FOURTH EDITION.

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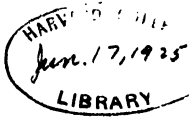


PREFACE

TO

THE FOURTH EDITION.

WHEN the first edition of this book was published it was intended to represent in some measure a reaction against the irregular 'test tubing' which prevailed in many chemical schools. The author is glad to know that the book has proved useful in the hands of many able teachers, and that his attempt to provide an elementary course of Chemistry which should afford training alike in method and theory has met with even greater success than he hoped.

It has been remarked that the writer employs the simple atomic symbols, in almost all cases, to indicate the elements which enter into chemical reactions, while demonstrating, by means of such experiments as number 29 and others, the two-atom structure of the molecules of a few of the elementary *gases*. The fact cannot be too strongly impressed on the student's mind that our present knowledge does not justify us in extending the use of the so-called 'molecular formulæ' for elements in the *gaseous* state (correctly

employed under experiment 29) to cases in which the elements concerned enter into the reactions in the state of *liquid* or of *solid.* Reactions of the latter class form the great majority of those commonly met with, and are best explained by equations which are free from unnecessary assumptions, but which adequately represent the relative atomic weights of the agents concerned in the chemical changes.

J. E. R.

March 1887.

PREFACE

TO

THE FIRST EDITION.

THIS work is identical in plan with my *Six Lectures on Experimental Chemistry*, but different in style, and much extended in range, so as to include the amount of knowledge of fact and principle usually expected from junior Arts, Medical and Pharmaceutical Students, as well as from the higher classes in Intermediate Schools.

The system pursued in this book is designed to lead the student through a series of connected experiments—often *quantitative* in form—and to assist him in the interpretation of his results, and in devising modes of testing the validity of the conclusions drawn from them. Thus while acquiring a tolerably wide knowledge of fact, the student receives a certain amount of training in the purely 'experimental method' of investigating Nature. If this training be sound, the study of Chemistry must prove a valuable means of mental education. How far the particular plan pursued in the following pages is likely to contribute to such a result, I must leave others to judge :

but a reviewer of my *Lectures* was so good as to say :—'In these Lectures the author departs widely from the usual routine of elementary treatises. . . . We believe that he is right in the plan he has adopted, and that instruction of this nature would greatly facilitate the acquisition of clear and distinct ideas of the leading facts and laws of Chemistry.' (*Chemical News*, vol. xxix. page 227.) This work is divided into four parts, each one being, as far as practicable, complete in itself. Part I. is introductory, and deals with first principles, and with the chemistry of the typical elements, hydrogen and oxygen, and their compounds; Part II., with the rest of the non-metals; Part III., with the metals; and Part IV., with organic chemistry. The experiments described are, whenever possible, those easily performed; in some cases, however, methods are necessarily detailed which the student may not have either the skill or the means to carry out, but he should endeavour to see these operations carefully conducted. It is assumed throughout that the reader can obtain some practical instruction in glass working and the construction of apparatus.

It is only necessary to add that the complete work will contain the solutions of all the problems in my *Lecture Note Book*.

J. E. R.

CHEMICAL LABORATORY,
TRINITY COLLEGE, DUBLIN:
November, 1880.

CONTENTS.

CHAPTER I.

PAGE

Preliminary experiments—Difference between physical and chemical change—Modes of effecting chemical change—Chemical attraction –Mechanical mixtures and chemical compounds 1

CHAPTER II

Experiments with Silver Nitrate and Magnesium—The chemical balance—Law of constant composition—Law of definite proportions 12

CHAPTER III.

Experiments with Magnesium and Hydrogen—Equivalents—Chief characters of Hydrogen gas . . . 21

CHAPTER IV.

Experiments with Hydrogen and Oxygen gases—Composition of water—Electrolysis—Chief properties of Oxygen—Combustion of candle in air 30

CHAPTER V.

PAGE

Experiments with Hydrogen and Oxygen continued—Specific gravities of gases—Effects of changes of temperature and pressure on gases—Avogadro's law—Dual character of elementary molecule—Gay-Lussac's laws—Atoms—Atomic weights of gaseous elements determined—Atomic Theory 44

CHAPTER VI.

Experiments with Silver, Copper, and Magnesium—Capacity for heat—Specific heat—Dulong and Petit's law—Atomic heat 56

CHAPTER VII.

Table of Atomic weights—Distinction of metals and non-metals—Electro-chemical changes—Chemical formulæ, how deduced—Empirical and rational formulæ—Atomicity or quantivalence—Equations . . . 63

CHAPTER VIII.

Experiments with Acids, Alkalies, and Salts—Bases—Classes of acids—Radicles of salts—Simple and compound radicles 80

CHAPTER IX.

Further experiments with Hydrogen—Preparation—Properties—Flame tests—Hydrogen as a reducing agent—*Fer réduit* 86

CHAPTER X.

PAGE

Experimental determination of the volume occupied by one centigram of Hydrogen gas—Correction of gaseous volumes—The VOL—Calculations—Absolute temperature—Law of Charles 95

CHAPTER XI.

Further experiments with Oxygen gas—Preparation—Properties—Oxides—Acid producing and basic Oxides or Anhydrides—Indifferent Oxides—Oxyhydrogen flame—Ozone — Preparation — Characters—Allotropism—Isomerism 108

CHAPTER XII.

Experiments with water—Purification of water by distillation—Latent heat of steam—Effects of cold on water—Maximum density of water—Latent heat of water—Solvent action on solids, liquids and gases—Water supply—Hardness of water—Mineral springs—Sea water—Peroxide of Hydrogen—Preparation—Properties—Detection of—Test for *blood*—Hydroxyl—Law of Multiple Proportions 125

APPENDIX.

Modes of chemical change—Laws of Berthollet . . 143

INTRODUCTION

TO

EXPERIMENTAL CHEMISTRY.

PART I.

CHAPTER I.

PRELIMINARY EXPERIMENTS.

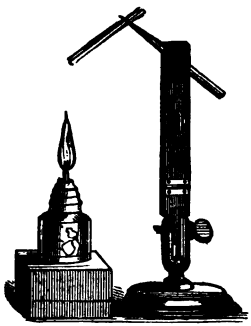
CHEMISTRY has for its object the discovery of the laws which govern the *composition* of all material things, and the action of one kind of matter upon another in all cases involving change in composition. This knowledge is acquired by experiment, accurate observation of the phenomena presented during an experiment, and careful reasoning upon the result. The following pages contain numerous illustrations of the application of this experimental method of inquiry in the study of chemistry.

Experiment 1.—Let us commence our course with a simple experiment.

Hold by means of a small pincers or tongs a piece of thin wire of the metal platinum in the flame of a

spirit lamp, as in fig. 1, or in that of a Bunsen gas-burner. Observe that the wire soon becomes red-hot and glows as long as it is held in the flame; but, when removed and allowed to cool, it resumes its original appearance, and if weighed before and after the experiment, no difference is observed. Therefore the change from cold to red-hot platinum is but a *temporary* one, the metal remaining unchanged in form and substance.

FIG. 1.



Experiment 2. — Now make an identical experiment with a piece of magnesium wire or ribbon. Observe that the metal soon begins to burn and emits much light, even when removed from the source of heat. It also gives out white fumes and leaves a white substance behind which, though retaining some of the form of the original wire or ribbon, can be easily powdered when cold, and is seen to be utterly unlike the metal which produced it. Moreover, the white substance is found to *weigh more* than the magnesium originally taken. In this case, a change has taken place on heating, and it is *permanent*.

The temporary alteration of the platinum wire is not accompanied by any difference in composition, and is spoken of as a *physical* change; that of the magnesium, as a *chemical change*, and the action, as

chemical action, because a material alteration in composition has taken place, as shown by the gain in weight; and a new body has been produced, evidently possessing characters which serve to distinguish it completely from the metal magnesium, and, indeed, from all other known substances.

All observed changes in matter can be placed in one or other of the above classes, but it is with chemical change and chemical action that we are principally concerned.

In the experiment with magnesium it was found that the application of *heat* served to bring about chemical change, but we shall note as we proceed that chemical action can be determined by other agents—namely, by *Mechanical force*, *Light*, *Electricity*, and a peculiar force called *Chemical attraction*, or 'affinity,' which acts only at excessively minute distances.

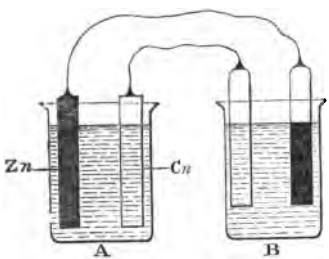
Experiment 3.—Place two or three small crystals (not more) of the salt called potassium chlorate in a stone-ware mortar, powder the substance and add half as much sulphur, also in powder. Mix gently and then give the mixture a sharp blow with the pestle. A report follows, indicating that chemical action has taken place, in this instance determined by *mechanical force*.

Experiment 4.—Again, dissolve a few crystals of silver nitrate in half a test tube of water and paint the liquid over some ordinary writing paper in a darkened room. Then divide the paper into two parts: preserve one in a drawer, and immediately expose the other to full sunlight or diffused daylight. The exposed paper will shortly discolour and assume

a chocolate brown tint, or even a bronzy black colour —the result of chemical change brought about by the agency of *sunlight*, for the paper preserved from light does not suffer any apparent change in the same time. The art of photography depends upon similar changes brought about by light.

Experiment 5.—Now take the little galvanic cell described at page 6 (see fig. 2, A) and attach a small slip of sheet platinum to the end of the wire from *Zn*, and connect a slip of copper with *Cu*; dip both in a strong solution of copper sulphate contained in B. Remove the slips after a few minutes and observe that a reddish deposit has formed on the slip connected by wire with the zinc plate *Zn*, of the cell. If the action be continued for some hours, a considerable layer of red metallic copper is obtained on the slip as the result of chemical change determined by *electricity* in the solution of copper sulphate. The art of electro-typing depends on this power exerted by electricity.

FIG. 2.



Experiment 6.—Finally, if we add to a small globule of the liquid metal mercury, or quick-silver, contained in a mortar, a few fragments of iodine, and mix them together with the pestle, the metal and iodine gradually disappear and a powder is formed. If the proportion of iodine used be large,

the resulting powder is red in colour; if little iodine be employed, the colour is a dull green. Here the two bodies named produce a new substance when brought near to each other, and this change is alone due to the *chemical attraction* of one body for the other. The exercise of this attractive force is facilitated by the liquidity of the metal, and the change is hastened by the addition of a few drops of spirit of wine, which dissolves some of the iodine and thus enables the particles of the latter to move more freely. This chemical attraction differs from other forces in the important particular that it only acts at excessively minute distances. This may be further illustrated in the following way :—

Experiment 7.—Mix in any dry glass vessel, such as a beaker or a tumbler, a tea-spoonful of 'bread soda,' or sodium bicarbonate, and the same quantity of finely powdered tartaric acid.[1] However closely the solid particles are brought together by stirring or rubbing, no action takes place, provided the mixture is dry. Add now some water to the powder, and violent effervescence ensues, indicative of chemical action. Water added to the acid or the soda *separately* does not cause any effervescence and merely dissolves each body, the violent action observed on addition of water to the mixed powders must therefore have been due to the mutual attraction of the two solids leading to chemical action; but that action could only take place when, by solution in water, the particles of each body were endued with greater mobility than in the

[1] Or the contents of the two papers sold as 'Seidlitz powder' may be mixed instead of the above.

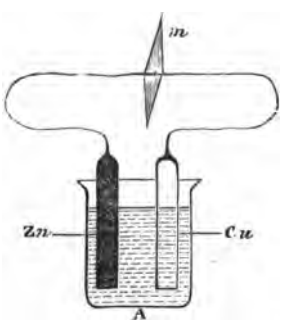
solid state, and were thus enabled to get within the sphere of each other's attraction.

We thus learn that chemical action is greatly facilitated by the solution or liquidity of one or all of the bodies engaged. We shall find later on, Experiment 53, that a fine state of division of a solid tends to a similar result.

In some of the experiments already cited, the student will have observed the evolution of *heat* and *light* during chemical action. Thus, when the magnesium wire burned in air, much heat and an intense light were produced. But *electricity* is also freely developed in certain chemical actions, and in fact the source of electricity in an ordinary galvanic cell is chemical action.

Experiment 8.—The simplest form of galvanic cell may be easily made thus:—Take a glass vessel, such as a tumbler (A, fig. 3), and fill it about two-thirds with water, to which one-tenth part of oil of vitriol (sulphuric acid) has been added. Next cut a slip of clean sheet zinc, *Zn*, a little longer than the glass; its width may be equal to half the diameter of the vessel. Make a hole through one end of the slip, pass a piece of bright copper wire through it and fasten securely by twisting the wire. Prepare

FIG. 3.



a similar slip of clean copper, *Cu*, with its wire, and the apparatus is complete. When the two wires are connected, as shown, and the plates immersed in the liquid, *without touching one another*, the zinc alone dissolves in the acid, the copper not being chemically acted on, while a current of electricity flows along the wire, and may be easily detected by bringing the wire over and parallel to the magnetised needle, *m*, of a toy compass. The needle tends to set itself at right angles to the wire, but if the chemical action be stopped, by taking the plates out of the liquid, and the connecting wire be brought over the needle as before, no motion takes place, as the wire no longer conveys electricity. The compass needle, therefore, serves as a detecter of electric currents circulating through copper wires.

When two or more of such simple galvanic cells as that just described are joined, usually in such a way that the zinc plate of one cell is coupled with the copper plate of the next, a *galvanic battery* of the simplest kind is obtained; but for details concerning galvanic cells and batteries, a work on Physics must be consulted.

Again turning to the experiment with burning magnesium, we find that it is capable of affording us another item of information. We pointed out that the white substance produced when the metal burns weighed *more* than the magnesium originally taken. In this case, then, heat enabled the magnesium to take to itself some other body which could only be derived from the air in which the metal was heated. The chemical action thus induced by heat was one of

combination, or the union of unlike kinds of matter.

Experiment 9.—The same agent—heat—is capable of effecting the reverse change. If we take a small quantity of the well-known white, crystalline and transparent substance called *silver nitrate*, and heat it gently in a small dry test tube, the body is seen to melt to a yellowish liquid, and, on continuing the heat, bubbles rise through the liquid and ruddy fumes pour out of the mouth of the tube. If we continue to heat until all action is over, and break the tube when cold, the residue is seen to consist of pure white metallic silver. In this case the chemical action brought about by heat resulted in *decomposition*, or resolution, of the silver nitrate into the metal silver, and some other kind of matter seen to be driven off as coloured vapour or gas.

Since chemical action may result either in *combination* or *decomposition*, it follows that chemical substances may be conveniently divided into two great groups: first, those forms of matter which do not suffer decomposition by the exercise of any force at our command; and, secondly, those bodies capable of resolution into some two or more members of the first group. The forms of matter included in the first group are called *elements*, and those in the second, *compounds*. The decomposition of a compound into its elements is spoken of as a process of *analysis*, and the production of a chemical compound from its elements is termed *synthesis*.

The researches of chemists up to the present time have made known to us some seventy elements. The

names of the most important of these are given in the table, which will be found at page 64. But it is necessary to guard carefully against the idea that the 'elements' so-called are certainly simple bodies: we cannot at present prove them to be compounds—that is all we can say.

All known chemical compounds are the result of union between some two or more elements; but the important question now arises whether this union is in the nature of a mere mixture, or of something much more intimate.

Experiment 10.—Make a mixture of iron filings with about two-thirds of their weight of sulphur (the 'flour of sulphur' of the druggists). A greenish-grey powder results, but distinct particles of iron and of sulphur can be easily recognised in it, not only with the aid of a magnifying glass, but also by stirring some of the powder into a considerable quantity of water, when the heavy particles of iron fall quickly to the bottom of the vessel, while the lighter sulphur more slowly subsides and collects as a distinct layer. Or the iron can be still more easily separated from the sulphur by means of a small horse-shoe magnet. If the latter be passed through some of the powder, the particles of iron are attracted by the poles of the magnet, and attach themselves so firmly that the particles of sulphur—which are not attracted but are mechanically adherent—may be blown away, leaving the metallic iron behind.

The constituents of this mixture can therefore be separated by mechanical means. Moreover, its properties partake of those of iron and sulphur.

Experiment 11.—Now heat *very strongly* a portion of the original mixture in a tube of Bohemian or hard glass ;[1] note that the mixture becomes pasty and then glows for a short time. Cool and remove the resulting dark substance from the tube. When examined with a magnifying glass, no particles of iron or sulphur can be detected, if the mixture was sufficiently heated; moreover, it is not attracted, or but slightly, by the magnet, and therefore does not any longer contain *free* metallic iron. The iron and sulphur are no longer separable by mechanical means, and the properties of the body resulting from the fusion do not partake of those of free iron or free sulphur. In fact, the glowing observed on heating the mixture was due to chemical combination between the two elements, and the product of that union—a body termed iron sulphide—possesses a definite group of characters which not only serve to distinguish it from the free elements iron and sulphur, or a mixture of them, but from all other known bodies.

Experiment 12.—Mix twelve parts by weight of finely-powdered charcoal (a form of the element *carbon*) with sixty-four parts of sulphur, also in a fine state of division. The mixture is an opaque, almost inodorous, dull, yellowish powder that may be exposed to the air for an indefinite time without loss of weight or other alteration. Now obtain a specimen of the liquid termed 'carbon bisulphide,' which is a chemical compound of carbon and sulphur *in exactly the same propor-*

[1] A glass which fuses with great difficulty, and hence may be suitably used in operations requiring a temperature so high as to easily melt ordinary glass tubing.

tions as the mixture of the two elements already made. This liquid [1] is perfectly transparent and colourless, and has a most disagreeable smell, while it is so volatile that a few drops let fall upon a plate disappear in a very short time. We thus learn still more clearly that a wide difference in properties may exist between a definite chemical compound and a mere mechanical mixture of its constituents. The special properties of the elements can be easily recognised in the mixture, but not in the definite chemical compound, unless we decompose the latter and sever the union of its components.

Thus in effecting the synthesis of a new chemical compound from its elements, the philosophic chemist performs an operation which approaches more nearly than any other to a *creative act.*

[1] For the preparation of this body see Part II. page 198. It must be handled with care, as it is very inflammable.

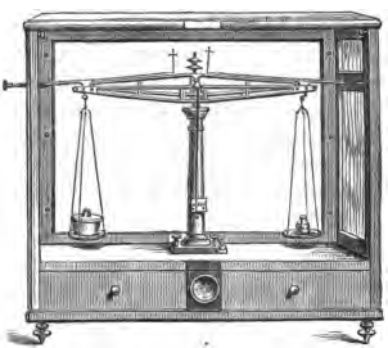
[NOTE FOR THE STUDENT.—Make a careful *précis* of the conclusions drawn from the data, and of the statements made in this chapter. This is an excellent practice, and should be continued throughout the work, as it serves to keep the *results* clearly before the mind.]

CHAPTER II.

EXPERIMENTS WITH SILVER NITRATE AND MAGNESIUM.

A KNOWLEDGE of the chief Laws of Chemistry can be more simply and naturally attained by the study of chemical *compounds* in the first instance than by the detailed examination of simple bodies or elements,

FIG. 4.



and the most easily managed compound with which the beginner can experiment is SILVER NITRATE.

It has been already proved by Experiment 9 that Silver Nitrate is resolved into metallic silver and coloured gas, when strongly heated in a glass tube.

Let us now examine this case of *decomposition* with the aid of a balance or delicate scales, one of the best forms of which valuable instrument is represented in fig. 4.[1]

Experiment 13.—Break up in a perfectly clean mortar some clear and pure *crystals* of silver nitrate ;[2] then press the powder between folds of white blotting-paper, in order to remove any trace of moisture. Next take a stout test tube of *hard* glass, measuring 12 centimeters long and 12 millimeters in diameter ; take care that it is clean and dry; then place it on one pan of the balance and counterpoise by placing a small pill box on the other pan, and adding grains of shot or pieces of tinfoil until equilibrium is established. Next place on the pan, along with the shot or foil, weights representing 170 centigrams (=1·7 grams), and now pour into the test tube on the other pan the powdered silver nitrate until the weights are balanced. The test tube then contains 170 centigrams of the silver compound. Now support the tube in a slanting position in the wooden clip shown in fig. 1, and gently heat the bottom of the tube with a spirit lamp, or a Bunsen gas-burner of the form shown in fig. 5. The silver nitrate melts quietly to a

[1] Much cheaper balances than that figured can now be obtained, which will indicate less than 1 milligram when loaded with 25 grams. When the student cannot obtain the use of a balance, he should perform the experiments as described without weighing the materials or products.

[2] The crystals are alone certain to give satisfactory results, as the 'Lunar Caustic,' sold in sticks, is sometimes adulterated and often impure.

clear liquid. If the temperature be now increased by bringing the flame closer, slight effervescence is observed—due to the escape of bubbles of gas. Soon reddish brown fumes appear, and these pass away into the atmosphere, while the residue in the tube loses much of its transparency owing to evident deposition of solid matter. The heating must be continued in such a way as to prevent any loss by spirting solid particles out of the tube, and until the ruddy fumes are completely dissipated and pure silver alone remains; finally, let the flame play on the sides of the tube so as to ensure the decomposition of any particles of the nitrate that may have yet escaped the full action of the heat.[1] When cold, replace the tube on the pan of the balance and adjust the weights on the other pan so as to restore equilibrium; the weights required represent the pure silver thus obtained from 170 centigrams of silver nitrate.

Two separate experiments made in the way described afforded the following results :—

Weight of metallic silver obtained from 170 *centigrams of pure silver nitrate.*

1st experiment	.	108·22 c. grs.
2nd „	.	108·40 c. grs.

The second experiment was made by a young student but little skilled in chemical manipulation.

[1] The *ultimate* decomposition may be thus represented :—

$$Ag\,NO_3 = Ag + NO_2 + O.$$

Now, it is found that the more carefully the experiment is made, the nearer does the result approach to 108; we may therefore say that 170 c. grs. of pure silver nitrate contain 108 c. grs. of the metallic element silver. Whatever may be the source of the silver nitrate taken, provided the compound be pure, and whatever the quantity employed in the experiment, provided the decomposition be carefully conducted, the weight of metal left after heating is always in the ratio of 108 to 170 of the silver nitrate employed. Thus we learn,

1st. That pure silver nitrate is a compound body.

2nd. That 170 parts of it contain 108 of pure elemental silver.

3rd. That it is *constant in composition.*

These are facts: the inference clearly to be drawn from them is that CHEMICAL COMPOUNDS GENERALLY ARE CONSTANT IN COMPOSITION. This inference is completely borne out by further experiments in the same direction, for it has been found that every chemical compound which possesses a group of characters serving to define it, and so to distinguish it from all other forms of matter, exhibits the remarkable constancy of composition just detected in the case of silver nitrate.

Upon this great principle, often termed the 'First Law of Chemistry,' the science really rests.

The admission of the constancy in composition of chemical compounds leads us to expect that chemical *combination* takes place in *definite proportions*, else it were impossible to obtain an adequate explanation of the fact that the constituents of such a compound as silver nitrate are always to be found in the body

in fixed proportions. We can put this conclusion to the test of experiment in the following way :—

Experiment 14.—Dissolve two or three medium crystals of silver nitrate in half a test tube of water, and throw in a small slip of magnesium ribbon. Now observe that the magnesium soon becomes coated with a dirty grey material which can be readily detached on shaking, and then falls quickly to the bottom of the tube. As the powdery substance is shaken off the slip, a fresh coating forms which can be again detached by shaking, leaving the magnesium thinner each time. This goes on until one of two things happens: either the magnesium slip disappears altogether, leaving the powdery deposit behind it if a relatively large quantity of silver nitrate [1] was taken in the first instance ; or, if the silver nitrate was used in a relatively small proportion, the magnesium slip no longer becomes coated and may be allowed to remain in the liquid without undergoing any further change.

We have next to examine the grey substance. Remove the magnesium slip, if any remains, and then pour off the clear liquid and drain it away from the

[1] In this case the clear liquid should still contain some unchanged silver nitrate in solution. To test for this, add to some of the clear liquid, poured off into a test tube, a few drops of solution of common salt. If the fluid becomes milky and lets fall a white *precipitate*, silver is present. This *test* for silver depends upon the fact that silver easily unites with another element, chlorine, and forms therewith the insoluble body termed silver chloride, which separates out. Common salt contains the necessary chlorine, and thus acts as a *reagent* for silver. For an equation representing this change see page 143.

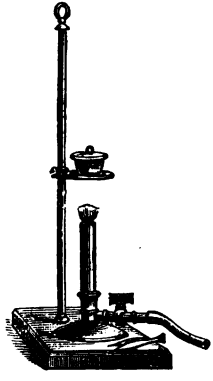
grey deposit as much as possible. Now take out some of the moist matter with a glass rod and place it on white blotting paper. If dried near a fire, the deposit becomes lighter in colour and appears as a fine powder, which, when rubbed with a polished knife blade, assumes a silvery lustre. By this means, and by chemical tests which will be described later on, this powder can be shown to consist of pure metallic *silver* in a very fine state of division. We conclude, then, that magnesium acts chemically on the silver nitrate in solution and decomposes it, precipitating metallic silver, while the metal magnesium disappears, evidently owing to solution in the liquid.

By a slight modification of the above experiment we can find the weight of pure silver deposited during the complete solution of a given weight of pure magnesium.

Experiment 15.—For this purpose, dissolve about 200 c. grs. (=2 grams) of pure silver nitrate (the precise quantity is immaterial) in about twenty cubic centimeters of distilled water contained in a perfectly clean porcelain crucible, which latter has been gently heated over the lamp flame to dry it, and then, when cool, counterpoised in the way already described in the experiment with the glass tube. Now take a piece of carefully cleaned and bright magnesium ribbon weighing about 10 centigrams—the exact weight must be accurately ascertained—and add it to the contents of the crucible, stirring the magnesium about occasionally with a short piece of glass rod, which latter must not be removed from the crucible until

the experiment ends. Silver separates as before, and after some time all traces of the magnesium disappear. The mixture is now allowed to stand for a short time, in order that all particles of the heavy silver may settle to the bottom, as much as possible of the clear liquid is then carefully poured away without disturbing the precipitate of silver. Some 20 or 30 cs. of distilled water are now to be added to the deposit, the latter well stirred up with the fresh water and then again allowed to stand, when the clear liquid may be decanted off as before without loss of silver. This process of 'washing by decantation' of the silver must be repeated five or six times in order to secure the complete removal of all soluble impurity from the metal. The crucible with its moist contents is next placed in a warm place to dry, and is then carefully heated over the spirit or gas lamp, as in fig. 5, for a few minutes, in order to ensure the removal of all traces of moisture. When cold, the crucible with the silver is replaced on the balance pan and the weight of the metal accurately ascertained.

FIG. 5.



An experiment performed as described afforded the following result :—10 centigrams of magnesium were added to 200 c. grs. of silver nitrate in solution, and the silver, collected after the magnesium had wholly disappeared, was found to weigh 88 c. grs.

By the following simple calculation we can find the weight of magnesium required to precipitate 108 c. grs. of silver from 170 c. grs. of the silver nitrate, in order to bring the statement of our result into harmony with that of the former quantitative experiment :—

$$88 : 108 . \therefore 10 : 12{\cdot}2.$$

However frequently we repeat and vary the form of the above experiment, we find that for 108 c. grs. of pure silver, removed from a solution containing an excess of the nitrate, 12·2 c. grs. (or 12 c. grs., if the materials are absolutely pure) of metallic magnesium dissolve. In other words 12 c. grs. of magnesium exactly replace 108 c. grs. of silver contained, as we have already seen, in 170 c. grs. of silver nitrate. There is therefore no doubt that metallic magnesium and silver nitrate act upon one another, or interact, in DEFINITE PROPORTIONS. All similar experiments have led to precisely the same result, hence the 'Second law of chemistry :'—

'ALL CHEMICAL SUBSTANCES INTERACT IN DEFINITE PROPORTIONS BY WEIGHT.'

The change on heating silver nitrate was one of *decomposition*, for 170 c. grs. of the compound broke up into 108 c. grs. of silver, and 62 c. grs. of the volatile matter we may provisionally group under the term 'nitrate;' but *combination* also, between the silver and the 'nitrate,' must have originally taken place in definite proportions.

Again, the change consequent upon the action of magnesium on silver nitrate was one of decomposition, *and* of combination, for while the silver nitrate was

decomposed and its silver separated just as completely as by heating the body alone, the 12 c. grs. of magnesium *combined* with the 62 c. grs. of 'nitrate,' and in fact the solution could be shown to contain at the end of the experiment magnesium nitrate weighing 74 c. grs. (12 + 62 c. grs.), for that weight of the new compound thus formed could actually be separated from the liquid.

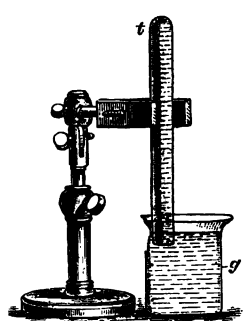
CHAPTER III.

EXPERIMENTS WITH MAGNESIUM AND HYDROGEN.

Experiment 16.—Half fill a test-tube with water to which two or three drops of oil of vitriol (sulphuric acid) have been added. Now plunge into the liquid a slip of magnesium ribbon and note the result. Brisk effervescence takes place, and the metal speedily disappears. The effervescence must be due to the escape of *gas*, and if we bring a flame to the mouth of the tube the gas takes fire and burns with slight explosions, but emits very little light while it burns.

Therefore magnesium, which displaces metallic silver from silver nitrate, causes the evolution of an inflammable gas from acidulated water. The next step is to collect some of this gas and examine its properties.

FIG. 6.



Experiment 17.—Take a glass tube closed at one end and about 20 centimeters long, and 2 centimeters in diameter, *t*, fig. 6; fill it completely with water acidulated with $\frac{1}{30}$th of its bulk of sulphuric acid; then place a piece of cardboard, or better, a ground glass plate, over the mouth of the tube and

invert it. Next bring the mouth under the surface of a larger quantity of the acidulated water contained in the wide glass beaker, *g*, and support by means of the stand s.

So long as the mouth of the tube is under the surface of the liquid no air can enter, as the water is retained in the tube by atmospheric pressure. Now take a piece of magnesium ribbon about 20 centimeters long, crumple it up and rapidly pass it through the water and under the mouth of the inverted tube. It will ascend into the tube and cause effervescence as before, but the gas cannot escape into the air and therefore collects in the upper part of the tube, while it displaces a corresponding volume of water. As the magnesium dissolves add fresh pieces until the tube is filled with the gas.

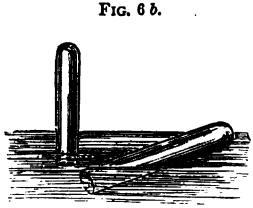
Pass the plate under the water and close the mouth of the tube, then detach the latter from the stand, remove the tube, still closed with the plate, from the water, and examine the contents.

a. Note that the gas is free from colour.

b. Turn the mouth of the tube up quickly and apply it to the nose. No peculiar odour is perceived.

c. Refill[1] the tube with gas as before, and apply a

FIG. 6 *b*.



[1] Instead of refilling the large tube, the charge of gas collected in it in the first instance may be transferred to three small test tubes, if the latter are filled with water in a large dish or trough, inverted and held with the mouth of each under the surface of the liquid. The large tube of gas is carried to the water, and the mouth brought under one of the

flame to the mouth. The gas takes fire and burns with a pale blue flame.

d. Again fill the test tube with gas, turn the mouth of the tube *upwards* and remove the thumb. After a few seconds bring a flame to the mouth of the tube. No combustible gas is found in the tube.

We are, therefore, warranted in stating that the gas produced when metallic magnesium acts on acidulated water is *colourless* and *inodorous*. We may further assert that it cannot be soluble in water to any extent, as we are able to collect it easily over that liquid; indeed, it can be easily shown to be *almost quite insoluble* in water. It is *combustible* and is *much lighter* than atmospheric air, as evidenced by the rapidity with which it escapes on holding the tube with its mouth directed upwards. The gas possessing these properties chemists call HYDROGEN, and regard it as an elementary body.

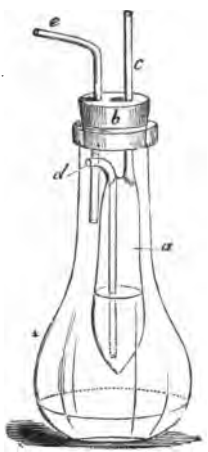
Although hydrogen is an extremely light body—in fact, the lightest known form of matter—it admits of being weighed like all other material things, whether gases, liquids, or solids. Hence we can next set to work in order to answer the important question, What weight of hydrogen do 12·2 centigrams of magnesium displace from acidulated water?

Experiment 18.—With the aid of the apparatus shown in fig. 7 an answer to this question can be easily obtained.

test tubes as shown; on inclining the large tube gas will pass from the latter up through the water and be caught in the test tube. Several tubes may thus be filled with gas from a single large vessel.

The flask A should be very light, and of about 50 cubic centimeters capacity; the little glass apparatus *a* should also be very light, and its tubes *c* and *d* must be fused into the glass. The tube *e*, like *c* and *d*, is open at both ends, but that within the apparatus need not project into the flask as shown in fig. 7, but may be cut off close to the cork.

FIG. 7



In order to use the apparatus, fill the small inner flask *a* to the extent shown with strong oil of vitriol by removing the cork carrying the tubes and dipping *a* under some oil of vitriol, contained in a beaker, until the mouth of *d* is beneath the surface of the liquid. Suction applied at *c* causes the acid to enter to the desired extent, when the apparatus is removed from the acid, washed well externally with water so as to remove all acid from the exterior of *a* and from the mouth of the tube *d*. Before replacing the cork in A, drop into the latter exactly 12·2 centigrams of clean bright magnesium ribbon, along with the amount of water indicated in the sketch: then fix the cork in its place, plug the opening of *e* with a small piece of wax, dry the outside of the flask with a soft cloth, place it on one pan of the balance and accurately counterpoise the apparatus.[1]

[1] The apparatus, when ready for experiment, should not weigh more than 50 grams.

Next remove the flask to a sheet of clean white paper, slip a small piece of flexible tube over *c* and force air very gently into *a* until a few drops of oil of vitriol fall from *d* into the water in A containing the magnesium. Gas will soon be evolved, and this gas we already know to be hydrogen. It has no exit save through the tube *d*, and after bubbling through the oil of vitriol in *a* it escapes from *c* into the atmosphere. In its passage through the liquid the gas loses any moisture that it may carry with it, as the oil of vitriol possesses the convenient property of absorbing water with great avidity: hence only pure dry hydrogen, mixed at first with some air, escapes from *c*. As the evolution of gas slackens, a little more oil of vitriol can be forced over, and this operation repeated if necessary until the magnesium disappears. When this point is reached, remove the wax plug from *e* and place it on the balance pan, next apply suction to the flexible tube at *c*. Air is thus drawn in at *e* and replaces the last traces of the hydrogen thus sucked out and dried in its passage through *a*. The flask is wiped carefully, and replaced on the balance pan. It will now be found *lighter* than the counterpoise, indicating that it has lost matter during the experiment. The matter lost we know consists of the pure dry hydrogen gas, and the precise weight of it can be ascertained on restoring equilibrium by addition of weights to the pan on which the flask A rests.

When the experiment described is carefully conducted, 1 CENTIGRAM almost exactly restores equilibrium; therefore that is the weight of hydrogen

evolved during the solution of 12 centigrams of pure magnesium in acidulated water.

The results of the quantitative experiments hitherto performed may be stated thus, neglecting decimals :—

1	centigram	of HYDROGEN was separated by
12	c. grs.	„ pure MAGNESIUM, which also displaced
108	„	„ pure SILVER from
170	„	„ SILVER NITRATE.

The numbers so obtained are called *equivalents*, because they represent weights which are of *equal value* in chemical changes. In all such changes hitherto examined, hydrogen has never been found to directly displace or combine with *less than* its own weight of any other element or compound, or indeed with less than three times its own weight of any other form of matter: hence it is properly taken as the unit of a scale of equivalents which really includes all the simple and compound bodies known. On this scale, magnesium, silver, and the compound silver nitrate, occupy the positions assigned to them above, and these are the lowest values obtained in any experiments hitherto made.

A familiar illustration will probably render the meaning of the term 'equivalent' clear. A single brilliant diamond of purest water, weighing but one grain, has approximately the same *purchasing power* as the weight of

Gold represented by	. .	3 sovereigns.
Silver „	„ . .	60 shillings.
Bronze (an alloy of tin and copper), by 720 pence.		

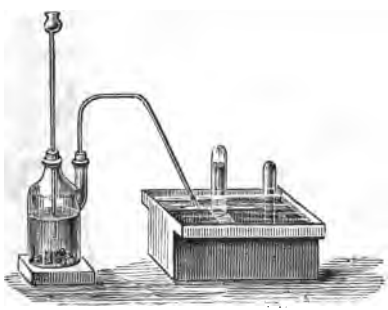
Thus a diamond of a certain quality will purchase more

than its own weight of any other substance: the *economic value* of a unit weight of diamond in exchange is therefore greater than that of any other material found in commerce. Similarly the *chemical value* of a unit weight of hydrogen in exchange is greater than that of any other element known to chemists.

As 170 c. grs. of silver nitrate are equivalent to 1 c. gr. of hydrogen, the student will now understand our reason for selecting the weight of the silver compound that we operated upon in the first quantitative experiment.

Experiment 19.—The most convenient method for the preparation of considerable quantities of hydrogen

FIG. 8.



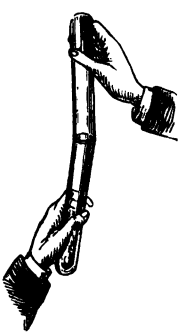
gas for experiment is the following. Take a glass bottle of the form shown in fig. 8, place in it some clippings of sheet zinc and sufficient water to occupy about one-third of the bottle Replace the cork and pour some oil of vitriol—about a teaspoonful—down the thistle funnel. Chemical action quickly commences and hydrogen gas is freely evolved; for zinc, like magnesium, easily dis-

places hydrogen from acidulated water—1 centigram of the gas being set free by 32·5 c. grs. or one equivalent of pure zinc. The gas is conducted by means of the glass delivery tube under the water in the 'pneumatic trough,' and it is there collected in glass jars or bottles previously filled with water and inverted, keeping the mouths under the liquid in the trough. A small shelf supports the jars over the delivery tube. It is advisable to allow the gas to bubble through the water for some time before collecting it in jars, or until the air is judged to be expelled from the gas bottle and its place taken by hydrogen, as the latter forms an *explosive mixture* with atmospheric air.

a. Remove a jar full of hydrogen from the water, keeping its mouth downwards. Take a piece of

FIG. 9.

FIG. 10.



lighted taper attached to a wire and pass it rapidly up into the jar, as shown in fig. 9. The gas takes fire at the mouth of the tube and burns there with a pale

blue flame, but the taper is extinguished ; on bringing it down to the mouth of the tube again, it can be re-kindled there. Therefore hydrogen, though a combustible gas, *does not support the combustion* of a taper which burns readily in air.

b. Take a dry glass jar, hold it with its mouth downwards and bring under it a jar full of hydrogen, carried from the trough with its mouth downwards. Now invert the jar of hydrogen, bringing its mouth under that of the dry jar, as shown in fig. 10. After ten or fifteen seconds remove the lower jar and bring the lighted taper under the upper one : a slight explosion occurs, and flame is observed, indicative of the presence of hydrogen ; therefore the latter body is so much lighter than air that it can be poured *up* through the latter, and will accumulate in the upper part of any vessel previously full of air.

c. The same point can be elegantly demonstrated by removing the gas delivery tube from the water, drying it, and introducing the end into the neck of a small collodion balloon. If any zinc remains undissolved in the generating flask, a few drops of fresh acid added through the funnel will hasten the evolution of gas, and the latter passing into the ballon will expand it. When fully distended, detach the balloon from the tube and set it free. It will ascend rapidly through the air of the room until arrested by the ceiling, and will remain there until much of the gas escapes and the residual hydrogen is no longer sufficient to buoy up the balloon. The latter then falls and may be reserved for another experiment.

CHAPTER IV

EXPERIMENTS WITH HYDROGEN AND OXYGEN GASES.

Experiment 20.—As we have already proved that hydrogen gas burns in air, we may evidently construct a small apparatus which can afford us a stream of the gas for combustion at a jet. The most convenient form is that represented in fig. 11. The gas delivery tube of fig. 8 is replaced by a short piece of straight tube, which passes through the cork of the generating bottle and through the cork of the wide tube, *t*, which latter is filled with fragments of calcium chloride, a powerful absorbent of moisture. Through the second cork of *t* there passes a small glass tube, drawn out so as to form a rather fine jet. The flask contains strips of zinc, and water, as before, and on pouring oil of vitriol down the funnel tube, hydrogen is evolved. Let the stream of gas issue freely from the jet for some time before a light is applied,[1] else an explosion will occur; then kindle the gas.

FIG. 11.

[1] It is well to cover the jet with an inverted test tube, and to remove the latter, mouth downwards, when it is desired to test the gas, and then to apply a flame to the test tube. If

a. Note that the hydrogen flame is of a pale bluish colour, and emits very little light; but it is intensely hot, for if we introduce a fine platinum wire into the flame it becomes nearly white hot, and emits much light.

b. If we take a glass tube, open at both ends, about one centimeter wide and 30 centimeters long, and pass the jet up into it, the flame is seen to suddenly elongate and a musical note results. The note emitted by this *chemical harmonicum* depends on the diameter and length of the tube; consequently tubes varying in these particulars may be used to produce different sounds.

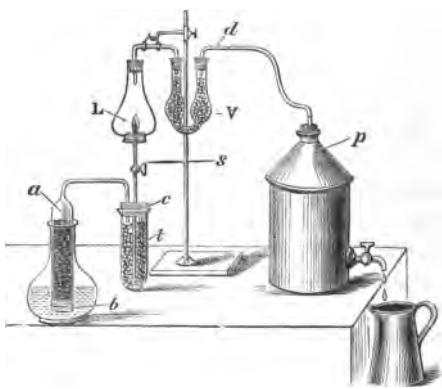
c. It will be observed in these experiments that the glass tubes are bedewed when they approach the hydrogen flame. Next place the flame under a large bell jar, or invert over it a large dry wide-mouthed bottle. The inner surface of the bottle is quickly bedewed with moisture, and presently drops of liquid trickle down the sides and collect at the shoulder. When some drops of the liquid have been collected, it can be examined, and is then found to possess all the properties of *water*. Now, since the calcium chloride in the drying tube completely removes moisture from the *unburned gas*, and the latter does not bedew a cold surface against which we may allow it to impinge, the liquid we observe to be deposited from the flame must be a product of the combustion of hydrogen in air, just as the white substance, see

the gas burns quietly, it may be safely kindled at the jet; but if with explosion, it is still unsafe, and the testing must be repeated after a few minutes.

Experiment 2, is a product of the combustion of magnesium in air. By means of the next experiment we can at least prove that the water produced in the combustion of hydrogen weighs *more* than the gas burned, and therefore that the process is one of chemical combination in progress between hydrogen and some constituent or constituents of atmospheric air; the resultant water is consequently a compound of hydrogen, or of the water generator (ὕδωρ, water; γεννάω, I generate), with some other kind of matter.

Experiment 21.—Take a U tube of the form of *a*, fig. 12, fill the wide limb very loosely with fragments

FIG. 12.



of zinc and insert the cork *b* which serves to prevent the zinc falling out when the tube is inverted, but which should be perforated so as to allow liquid to flow freely in and out. Pass the narrow limb of the U tube through a good cork *c* which fits a test tube

about 2 centimeters in diameter. The cork also carries the glass tube *s* provided with a fine glass stopcock which can regulate the supply of gas to the jet in which the tube terminates; the wide end of this tube is sufficiently large to pass through the cork *c* to the bottom of the test tube *t*. The latter is now filled with fragments about the size of a pea of dry and porous calcium chloride, and by turning the tube nearly on its side and tapping, the tube of *s* can be passed down along the glass and the cork inserted as shown. Now pass the wide limb of *a* through the neck of a light flask of about 80 or 100 centimeters' capacity, containing diluted sulphuric acid, and secure the tube *a* in the neck by means of slices of rubber cork, but without interfering with access of air. On turning the stopcock *s* the acid rises in *a* and acts upon the zinc, hydrogen is evolved and passes through the drying tube *t* before it can escape from the jet. The evolution of gas is allowed to continue until all air has been expelled, then the hydrogen can be kindled at the jet, and once it is found to burn freely, the stopcock is turned off, the evolution of gas ceases, because the latter has now no exit through *s*, and accumulates in *a*, forcing out the acid through the perforated cork *b*, and therefore away from contact with the zinc.

Before the experiment, the apparatus is accurately counterpoised, and a quantity of dry gas is then burned at the jet, under conditions to be presently described, and the stopcock again closed. If, when cold, the apparatus be replaced in the balance it will, of course,

weigh less than before, and the weight lost is the weight of dry hydrogen burned.

Another piece of apparatus is now to be prepared. This consists of a small paraffin lamp chimney, L, fig. 12, connected by means of a cork, as shown, with the U tube V filled with calcium chloride. This is our water collector, and is to be attached by the wire hook to the arm of a balance and carefully counterpoised before an experiment.

Conduct the experiment thus: counterpoise both pieces of apparatus and connect *d* by means of a flexible tube with an *aspirator*[1] *p*, as shown, so that a stream of air may be drawn slowly through the water collector during the combustion of the hydrogen. Now turn the stopcock *s*, immediately kindle the hydrogen, and pass the flame well up into the tube L. Water is produced during the combustion and collects chiefly in V. When the hydrogen has burned for some minutes, close the tap *s*, and stop the current of air through L; allow both pieces of apparatus to cool down completely, then disconnect and weigh each separately. The gain in weight of the drying apparatus represents the weight of water produced by the combustion of the weight of hydrogen burned at the jet *s*.

When the experiment just described is conducted

[1] A five-gallon oil can provided with a stopcock, as shown, and its mouth closed by a cork, carrying the inlet tube, forms an aspirator of a convenient size. The can is nearly filled with water at the outset; when the water is allowed to flow through the tap, air enters through the inlet to replace it, and thus a steady current can be drawn through any apparatus.

with great care, it has been found that *for every centigram of hydrogen burned almost exactly* 9 *centigrams of water are obtained* in the drying apparatus; thus it can be proved that the hydrogen gains in weight on undergoing combustion in air; and, further, that the product of combustion weighs 9 times as much as the hydrogen burned. For independent evidence on the same point see under Experiment 27.

The next step clearly is to resolve water into its constituents, or to decompose it, in order to isolate the matter which hydrogen must have obtained from air.

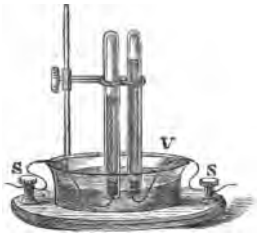
The compound water, whether in the liquid condition, or when gaseous (as steam), withstands a comparatively high temperature without decomposition;[1] similarly light alone is without action upon it, but electricity is found to decompose it with facility, and the current derived from a Grove's or Bunsen's galvanic battery consisting of two cells is sufficient for the purpose.

Experiment 22.—If we attach to the copper connecting wires of such a battery small slips of platinum (taking care that the connections are perfectly clean and bright), and then plunge the platinum terminals or 'poles' into some water acidulated with a few drops of oil of vitriol, in order to make it a good conductor for electricity, bubbles of gas are seen to rise from each pole. Note that more gas seems to be evolved at the pole connected with the zinc end of the battery than at the other. In order to collect the gas it is only necessary to arrange the apparatus shown in fig. 13. The vessel v contains the acidulated water. The two test tubes are filled

[1] At a white heat it suffers decomposition.

with some of the same water and then inverted with the mouth of each below the level of the water in the vessel V, and supported close together by clamps. The platinum poles are now arranged as shown, their wires being attached to the binding screws S, S, which latter are also connected with the battery. The wires are dried and then completely coated with sealing wax, from the platinum slip to the point *c*, so as to prevent any escape of electricity, except through the plates, when they are immersed in the water. Each platinum pole is then brought under the mouth of a test tube and secured in position. Gas bubbles arise from the poles as before, but instead of escaping into the atmosphere they collect in the tubes placed to receive them. A marked difference is observed in the amount of gas given off at each pole, and it is presently seen that when one tube is half full of gas the other is but quarter full.

FIG. 13.



In order to examine the gas in each tube, remove the wires, then close the mouth of the tube containing the largest volume of gas with the thumb passed under the surface of the water in the vessel V. Invert the tube, slip aside the thumb, and quickly apply a flame to the mouth of the vessel; the gas takes fire and burns with a pale blue flame, and this gas is hydrogen.

A similar experiment is made with the contents of the second tube, but the gas it contains does not take

fire. If, however, we dip into the gas a splinter of wood with a glowing tip, the wood bursts into flame, and active combustion ensues. This gas is, therefore, incombustible in air, but is a *supporter of combustion.* This body, like hydrogen, is an element and is called OXYGEN.

The process of analysis by electricity just used is termed *electrolysis*, and is often employed in effecting the decomposition of chemical compounds. During the electrolysis of water we have already observed that twice as much hydrogen is evolved as oxygen, and the presumption is that those are the proportions by volume in which the two gases unite to form water.[1] But we have not yet proved that water consists of hydrogen and oxygen *only*. If, then, we take the mixture of gases evolved from water, consisting, as we know, of two volumes of hydrogen and one volume of oxygen, such a mixture must be capable of reproducing water *if* the latter consists exclusively of these two elements in the proportions stated.

Experiment 23.—Take a stout wide-mouthed phial of about 100 c.c. capacity. Fit it with a caoutchouc cork and, having bored a hole axially through it, insert the short limb of the narrow but strong delivery tube bent in the form shown at *d*, fig. 14. The wider tube shown can be filled with fragments of calcium chloride when a supply of the dry gaseous

[1] 100 cubic centimeters of water dissolve only 2·989 c. cs. of oxygen at mean temperature and pressure, and 1·93 of hydrogen gas under the same conditions; the solubility of each gas is therefore so low and so nearly the same, that the above inference may be properly made.

mixture is required. Then pass two stout wires of platinum through the cork on each side of, and close to, the glass tube, and attach small slips of platinum foil to the ends of the wires that project within the bottle. Nearly fill the vessel with water containing a little sulphuric acid and insert the cork, connect the wires projecting from the cork with the terminals of the battery, as shown, and a steady supply of an electrolytic mixture of hydrogen and oxygen will be

FIG. 14.

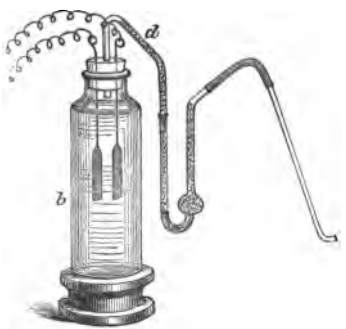
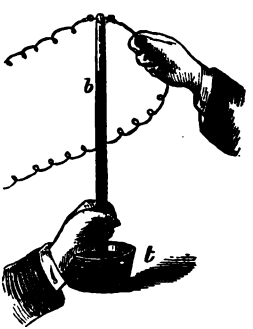


FIG. 15.



obtained. When it is judged that all air has been expelled from the bottle and tubes, collect some of the mixed gases in a small test tube over the liquid metal mercury, contained in a small and strong glass trough, as in fig. 15. This mechanical mixture of the two gases may be kept for an indefinite time without combination taking place, but if we remove the test tube from the trough and apply a flame to the mouth —a flash of light, and a rather violent explosion follow, indicating that chemical union has taken place.

We thus learn that combination of the gases can be determined by heating them sufficiently.[1]

Experiment 24.—A stout glass tube closed at one end is now taken ; it should be about 50 centimeters long and 1 centimeter in diameter. Two thin platinum wires pass through the sides and are sealed into the glass near to the closed end, and opposite to each other ; but their extremities within the tube must be kept at a very short distance apart. The object of this arrangement is to leave a gap so that an electric spark may be sent between the wires within the tube, and thus, by heating the mixture of gases, determine their combination. Such a tube is called a *eudiometer*, and must be stout so as to resist the force of the explosion that ensues ; it is shown at *b*, fig. 15.

Fill the tube with mercury, and when quite full, close the mouth with the thumb, and bring it under the surface of some more mercury, contained in the small trough *t*, fig. 15. Now half fill the tube with electrolytic gases from the apparatus shown in fig 14. Then remove the generator and pass a pad of india-rubber under the mercury and under the mouth of the tube. Press the pad against the bottom of the trough with the tube grasped firmly by the hand. When the tube is in this position, pass a spark from a coil, a Leyden jar, or a small electrophorus, through the gases by means of the wires sealed into the glass, one of them being connected with the earth by means of wire, the other with the apparatus that is to afford the

[1] See Chapter IX. for experiments with the oxyhydrogen flame.

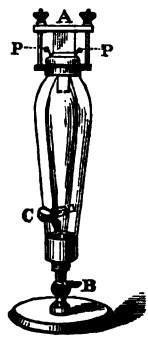
spark. A flash of light passes down the gas in the tube and a jerk is felt by the hand, and then all is over. On relaxing the pressure and moving the mouth of the tube from the pad, but keeping it under the surface of the mercury, the latter rushes up so as to fill the closed end almost completely; the gases have therefore been condensed,[1] or rather, the product of their union is not a gas, but must be either a liquid or a solid occupying an exceedingly small space as compared with that previously filled by the generating elements. If we examine the upper part of the tube carefully with a lens, we can detect between the mercury and the glass minute drops of liquid. This liquid can be proved to be *water. It is therefore certain that water consists only of hydrogen and oxygen, and that those elements combine to form water in the proportions by volume indicated by the results of electrolysis.*

Experiment 25.—A similar experiment to that just described may be performed with the apparatus shown in fig. 16, termed a 'Cavendish eudiometer,' because it was with such a vessel that the Hon. Henry Cavendish demonstrated the composition of water in the year 1781. The strong glass vessel, fig. 16, is provided with a glass stopcock C and a stopper through which wires of platinum P P pass, and this stopper is retained in the neck of the vessel by means

[1] As a matter of fact a small bubble of hydrogen remains after explosion; this is chiefly due to the loss of a little oxygen by solution in the water of the bottle *b*, fig. 14, and further by conversion of a very small proportion of the element into a body called 'ozone.' If all the oxygen were evolved as gas there would not be any free hydrogen after the explosion,

of the clamp A. The brass stopcock B allows the apparatus to be screwed to the plate of a good air-pump, and when exhausted of air, B and C are closed, and not opened until the tube is screwed to the brass stopcock of a bell jar similar to that shown in fig. 18, but containing some of the electrolytic gases. On opening the taps the mixture of gases rushes in to fill the vacuum. The stopcocks are again closed, the eudiometer screwed to its stand, and a spark passed through the mixture. A brilliant flash of light accompanies combination, and the sides of the glass vessel are bedewed with the water resulting from the combination of the gases.

FIG. 16.



The experiments hitherto made have led directly to the conclusions we have already drawn from them respecting the composition of water, but they also afford complete proof that *atmospheric air contains oxygen*; and we thus learn in addition that the great heat evolved during the combustion of hydrogen in air is due to the chemical union of hydrogen with the oxygen of the air. Finally, we are led to suspect that all ordinary cases of combustion which come under our notice are due to the rapid chemical combination of atmospheric oxygen with the body burned. Under Experiment 21 a method was described by which the weight of water produced during the combustion of 1 c. gr. of hydrogen can be determined, and it was stated

CHAPTER V.

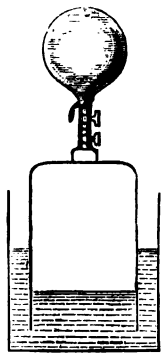
EXPERIMENTS WITH HYDROGEN AND OXYGEN GASES (*continued*).

WE now know positively that oxygen gas is a constituent of atmospheric air—though it is not the only one—and of water. The study of the composition of the latter has further made known the curious fact that oxygen requires twice its volume of hydrogen gas to form water, and only in this proportion does direct combination take place between those elements. Therefore the two gases unite in as definite proportions by volume as by weight, and it is evidently probable that an intimate connection exists between weight and volume combination in this case: hence we must investigate the point more closely.

Experiment 27.—The first step in this direction is to select a globe of about 1½ liters' capacity provided with a stopcock, and to exhaust it of air as completely as possible, by means of a good air pump, to the plate of which it can be screwed; then close the tap securely, remove and counterpoise carefully on the balance. The globe is next taken from the balance and connected, as shown, with a vessel containing pure hydrogen gas, and the stopcock opened; hydrogen rushes in and fills the globe. The stopcock is

again closed, after the levels of liquid within and without the jar have been equalised, and the vessel re-weighed. The increase in weight is that of the hydrogen which has entered. The globe is again exhausted to the original point as determined by the gauge attached to the pump, and again filled with gas, but this time with pure oxygen, whose weight is then determined. Now if care be taken to exhaust as completely as possible each time—certainly to the same extent—and that the bodies are pure, and the temperature does not vary so as to unequally expand or contract the gases, the weights obtained are those of equal volumes of the two gases. In a particular experiment conducted in this way the hydrogen weighed 11 centigrams, and the oxygen gas 174 centigrams. The *specific gravity* of oxygen as compared with hydrogen, or *the ratio of the weights of equal volumes of the two bodies*, when hydrogen is taken as the standard, and =1, is

FIG. 18.



$$\frac{174}{11}=15{\cdot}8,$$

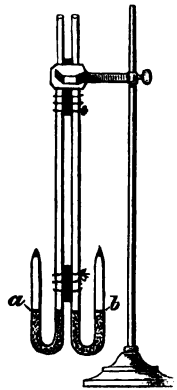
or as nearly in the ratio of 1 : 15·96—the true ratio—as can be expected in a rather rough experiment. Therefore oxygen gas may be said to be 16 times heavier than hydrogen. Now since one volume of oxygen requires two volumes of hydrogen for the production of water, it follows that 8 centigrams

by weight of oxygen must unite with 1 centigram of hydrogen to form 9 centigrams of water—a result identical with that obtained by the direct weighing of the water produced in the combustion of a given weight of hydrogen. Therefore, a very close connection exists between combination by weight and by volume.

It may be added that the specific gravities of all gases can be determined by the method just described, and since hydrogen is the lightest gas known, it is taken as the standard for reference.

The experiments already made with the two gases, hydrogen and oxygen, place beyond doubt the fact that they are perfectly distinct forms of matter as far as *chemical characters* are concerned, but they evidently resemble each other in certain *physical characters*, for they are both colourless, invisible, and inodorous. Let us now see whether this resemblance extends farther.

FIG. 19.



Experiment 28.—Take two tubes of as nearly as possible the same diameter and length. Close each at one end and bend to the form shown in *a* and *b*, fig. 19. The short limb may be about 20 centimeters, and the longer 1 meter, in length. Take one of the tubes, fill with water acidulated with dilute sulphuric acid and invert over the pole (fig. 13) from which electrolytic hydrogen is

being evolved; collect enough of the gas to about half fill the shorter limb of the U tube, then close the mouth with the thumb, remove and make the gas pass completely into the closed limb: this can easily be done by bringing the tube to a horizontal position while the shorter limb is uppermost. When the gas has been transferred, bring the apparatus into the position shown, and adjust the level of the liquid in both limbs of the U by sucking out the water in the long limb by means of a pipette with a flexible tube attached, which latter should be of sufficient length to reach nearly to the bend. Fill the second tube to the same extent and in the same manner with electrolytic oxygen, and tie the two tubes securely together as shown.

When the apparatus is plunged up to the point *a* in a large beaker nearly filled with water at the boiling temperature, the gases in the tubes are found to expand considerably. The expansion of the hydrogen is seen to be the same in amount as that of the oxygen. Similarly in cooling down again to the temperature of the air they contract equally.

We learn from this experiment that the two gases resemble each other in another particular, namely, that they are affected *to sensibly the same extent by equal alterations of temperature*, when observed under the same conditions.

Now replace the hot water in the beaker by some at the temperature of the room, and leave the tubes undisturbed for several minutes, in order that the gases may acquire the temperature of the water in the large vessel; then pour mercury into each wide tube until nearly full, and the column in each is of equal length.

Note that as the columns of mercury rise to the same level and as the pressure upon the gases equally increases, *the volumes contract to the same extent.*

If we remove the mercury, the gases expand equally and regain their original volume when the pressure is reduced to that at which we commenced.

Therefore hydrogen and oxygen gases, when compared under the same conditions, are affected in the *same way and to sensibly the same extent by equal alterations of pressure.* When the same mode of investigation is applied to other gases, whether elementary or compound, they are found to suffer very nearly equal changes of volume when subjected to equal variations of temperature and of pressure.

The conclusion to be drawn from all the data before us is that all gases agree in *physical constitution*, however much they may differ in *chemical composition.* This conclusion is independent of any hypothesis that may be founded upon the facts, but a most important one has been based on them by the distinguished physicist Avogadro. He assumed that all gases (as well as solid and liquid forms of matter) are made up of almost numberless, separate little particles, termed *molecules* (from *molecula*, a little mass), and that *equal volumes of gases contain the same number of molecules, when compared at the same temperature and pressure.* This is the statement of Avogadro's, or, as it is often called, Ampère's law, for to the last-named philosopher is due the credit of having specially drawn the attention of scientific men to the importance of the principle enunciated by Avogadro, when the statement of it made by the latter had been all but

completely overlooked. It follows from Avogadro's law that the ratio of the weights of equal volumes (containing equal numbers of molecules) of hydrogen and oxygen gases, compared at the same temperature and pressure, must represent the relative weights of the free molecules, or ultimate particles, of the two bodies. We have already found (Experiment 27) that a given volume of oxygen is sixteen times heavier than an equal volume of hydrogen under the same conditions : therefore the molecule of oxygen is sixteen times the weight of the molecule of hydrogen.

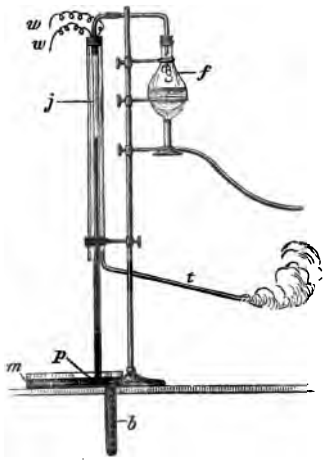
Let us proceed a step farther. We know already that one volume of oxygen and two volumes of hydrogen gas unite to form the compound water. We may now express the same thing in the following statement :—One molecule of oxygen unites with two molecules of hydrogen to form the compound water. But the question then arises whether one or more molecules of the compound water result from their union. We can obtain an experimental answer to this question in the following way :—

Experiment 29.—Take a eudiometer tube similar to that already employed in Experiment 15, 6 millimeters in diameter, and 80 centimeters in length, and fill it not more than one-third with the electrolytic mixture of oxygen and hydrogen as before ; now place over the tube the glass jacket *j* as shown, which is connected above by a cork with a flask *f*, in which water is boiled and by means of which the jacket can be filled with steam. The lower end of the jacket is also closed by a cork through which the eudiometer passes, and the side

tube *t* which serves to convey away the excess of steam.

When the gaseous mixture in the eudiometer is heated, it expands until it acquires the same temperature as the steam. When the mercury ceases to fall, mark its position in the tube by means of a flexible ring slipped over the jacket, and also measure as accurately as possible the height of the mercury in the tube over the surface of that in the trough *m*, then press the mouth of the tube firmly down on an india-rubber pad, *p*, passed under the mercury for the purpose, and explode the mixed gases as in the former experiment. This can readily be done if the wires fused into the glass sides of the eudiometer are connected with short wires which pass between the cork and the glass jacket, as at *w* and *w'*.

FIG. 20.



When the pad is removed from the mouth of the tube after the explosion, the mercury is seen to rise in the eudiometer; but, before measuring the amount of contraction that has taken place in the gas, it is necessary to restore the original pressure by depressing

the eudiometer in the well *b*, of the pneumatic trough, until the difference of level between the surface of mercury in the tube and in the trough is the same as before explosion; it will then be found on measuring the gas (water-gas) remaining in the tube that the contraction amounts to *one-third* of the original bulk of the mixed gases, while the temperature has throughout been maintained by the current of steam.

After explosion we can have but water-gas, or steam, in the eudiometer; but the steam is prevented by the high temperature and low pressure from condensing to the liquid form. We have therefore measured water-gas under the same conditions as the mixture of two volumes of hydrogen and one of oxygen before explosion, and found that the water-gas occupies the *same space as the hydrogen which generated it.*[1] Now if, as we have seen, the two volumes of hydrogen represent two molecules of that body, the two volumes of the compound water-gas must, according to Avogadro's law, represent *two molecules* of that body. The result may be stated thus in the form of an equation :—

Hydrogen	+	Hydrogen	+	Oxygen
1 molecule		1 molecule		1 molecule

= Water-gas	+	Water-gas.
1 molecule		1 molecule.

Reasoning upon this result, it is perfectly clear

[1] The comparison of the results of a large number of experiments of this order led the illustrious French chemist Gay-Lussac to the following generalisations :—1. Gases and vapours combine in simple proportions by volume. 2. The volume of a compound gas or vapour always bears a simple proportion to the volumes of gases or vapours from which it has been formed

that each molecule of water-gas so produced must contain oxygen, and, if the law of definite proportions be true, as we know it is, each molecule of water-gas must contain the *same* quantity of oxygen, consequently a semi-molecule of that body. Hence, though the free molecule of oxygen is not divisible by any known physical means, it divides under the influence of chemical attraction into two parts. Now the weight of oxygen corresponding to the semi-molecule of that body is the smallest quantity of it that takes part in chemical change, and as it cannot be further divided, even by chemical means, it is called the *atom*[1] of oxygen.

Later on we shall find that the molecule of hydrogen is also chemically divisible in two parts or atoms; but this dual structure of certain elementary molecules is only known to be true of the elements when in the state of *gas*.

Now, if the weight of the molecule of hydrogen be taken as = 1, the weight of the *atom* of hydrogen must be represented as = $\frac{1}{2}$, but since less than 1 part by weight of hydrogen is not known to act in chemical change, it is convenient to take 1 as the *atomic weight*, or weight of the semi-molecule, of hydrogen. The weight of the molecule of hydrogen is therefore = 2.

As we have already seen from Experiment 27, the oxygen molecule is sixteen times heavier than that of hydrogen; therefore, since the molecular weight of hydrogen = 2, that of oxygen must = 32, while the *atomic weight* of oxygen[2] is 16.

[1] ἄτομος, indivisible.

[2] The equation given on the last page may therefore be written in symbols thus: $2H_2 + O_2 = 2H_2O$, if we use the symbol O_2 to represent the oxygen molecule, and H_2 the hydrogen molecule.

If, then, we desire to know the *atomic weight* of an elementary gas, it is only necessary to find its specific gravity, *i.e.*, to weigh it as in Experiment 27 against an equal volume of pure hydrogen under the same conditions. The weight obtained, referred to hydrogen as the unit, is the atomic weight of the body.

But the information that our experiment affords us does not end here, for we can deduce from it the specific gravity of water-gas, referred to hydrogen as our standard.

We have already learned that two molecules of water-gas, which must contain the hydrogen in two molecules (*i.e.*, 4 atoms) of that body, and the oxygen in one molecule (*i.e.*, 2 atoms) of that element, occupy the same volume as two molecules of hydrogen. Therefore one molecule of water-gas occupies the same volume as one molecule of hydrogen. Now, one molecule of water-gas must have the relative weight 18 (16, weight of the semi-molecule of oxygen + 2, weight of the molecule of hydrogen) referred to the hydrogen molecule = 2 ; this gives the ratio of 9 : 1 ; therefore 9 is the specific gravity of water-gas compared with hydrogen gas as the unit.

It may be useful to add the following definitions :—

A *molecule* of an element or compound is the smallest portion of a body that can exist in the *free state.*

An *atom* of a chemical element[1] is the smallest portion of it that is known to take part in chemical change, and is almost invariably half the *gaseous* molecule.

[1] A chemical *compound* has not *atomic* weight.

An *equivalent* of an element or compound is its replacing or combining value compared with an unit weight of hydrogen.

The Atomic Theory of the illustrious philosopher, Dr. John Dalton, of Manchester, was one of the first substantial attempts [1] to account for the law of definite proportions that we have seen to so remarkably govern chemical changes, and we may now state the theory and the difference in form between it as enunciated by Dalton (in 1804–8), and as adapted to the present state of our knowledge. Dalton supposed, as Avogadro did, that with all matter a point can be reached at which further mechanical subdivison is impossible, and it was to these ultimate particles he applied the term *atom*—the atomic weight being a constant for each element. The molecules of the present day are the representatives of the atoms of Dalton, and we have already learned from our experiments that the molecule of an element, though physically indivisible as we suppose, can divide under the influence of chemical attraction into two—but rarely more or less than two—parts, and to each part we now apply the term *atom.* Dalton further assumed *that chemical action takes place only between the atoms of matter, and in proportions by weight which are determined by the relative atomic weights of the elements.*

In the Daltonian theory as thus modified we have an explanation of the law of definite proportions, but it is necessary to guard against the supposition

[1] The fundamental conception in the 'Atomic Theory' was distinctly enunciated by two Dublin chemists—Kirwan in 1783, and Higgins in 1789.

that the law of definite proportions *depends* on this hypothesis. As we have seen, the theory is founded on two assumptions, both reasonable, it is true, but which are not at present capable of direct proof. We may, therefore, use the theory as an important help in our inquiries, but not as a support on which we may rest in full confidence. If, however, we desire to go still farther, and to enquire how it is that these elementary atoms possess the power of uniting with each other, we must simply confess that this is one of the many mysteries that still lie hidden from the view of man.

CHAPTER VI.

EXPERIMENTS WITH THE METALS, SILVER, COPPER, AND MAGNESIUM.

IT is obvious that the method of weighing an element in the form of gas against the same volume of hydrogen, when we desire to determine atomic weight, is only applicable in those cases in which the element is either a gas at ordinary temperature and pressure, or in which it can be converted into gas, or vapour, at a moderate and manageable degree of heat. Neither silver nor magnesium can be vaporised at even moderately low temperatures: hence we must seek for some other mode than that above referred to of fixing their atomic weights. The *equivalent*, or replacing value of silver stated in terms of the hydrogen unit, we have already proved to be 108, and that of magnesium 12. Now it is evident that the atomic weight in each case cannot be *less* than those values, but it may be more, for we have already seen that in the case of oxygen the least weight of that body that takes part as a whole in chemical change (the atom) is *twice* the equivalent.

Experiment 30.—Make the following curious and instructive experiment. Take a five shilling piece [1]

[1] Although the coin is not pure silver, it is sufficiently pure for this rough experiment.

and fasten it securely to a piece of fine binding wire. Take a piece of copper of the *same weight* and thickness, and attach it to wire. Now, while holding the wires dip the two pieces of metal into some water boiling in a kettle, or other vessel. After ten minutes or so remove the pieces, let them drain for a few seconds and attach the wires to a rod. At first the metals are equally hot to the fingers, for they have evidently been heated to the same extent; soon, however, the silver will be cool enough to be held between the fingers, and to be pressed against a piece of phosphorus without igniting it, while the copper will be still too hot to hold, and will easily kindle a test of the same kind. The silver, therefore, cools more rapidly than the same weight of copper under the same conditions. As the two metals do not differ materially in conducting power, we infer from this experiment that silver at 100° C. (the temperature of boiling water) contains less heat than the same weight of copper at the same temperature—in other words, a less *quantity* of heat is required to raise the temperature of a given weight of silver to the same extent as an equal weight of copper, hence the *capacity* of copper for heat is greater than that of silver.[1] If we could conveniently replace the

[1] That is to say the *specific heat* of copper is greater than that of silver. Water has the greatest capacity for heat of any liquid or solid, and the heat capacity of other bodies is referred to that of an *equal weight* of water as unity: thus the capacity of silver for heat is about $\frac{1}{17}$th that of an equal weight of water, the precise ratio being ·05701 : 1. This ratio is the *specific heat* of silver. The *atomic heat* of an element is

copper by the same weight of magnesium, the difference in rate of cooling would be still more marked. This difference amongst solid bodies in capacity for heat has long been known, but it remained for two eminent French physicists, MM. Dulong and Petit, to point out the fact that the elements having the highest equivalents are those of the lowest capacity for heat, and *vice versâ*, and they showed from numerous observations that *the heat capacity of an element is inversely as its equivalent.* This 'law of Dulong and Petit' attracted comparatively little notice until Professor Cannizzaro modified the statement of it, and drew attention to its great value as serving to aid the determination of the atomic weights of many of the solid elements. The law, as it now stands, may be stated thus:—*The atoms of elementary matter have the same capacity for heat.*

If this law be true, 108 centigrams of pure silver and 12 centigrams of pure magnesium when heated to 100° C.—the temperature of boiling water—and then allowed to cool, ought to give out on cooling to the same extent *the same quantity of heat*, if the above numbers represent the relative weights of their atoms.

By the method now to be described this test can be applied to the two metals.

Experiment 31.—The *atometer*, fig. 21, is really a large spirit thermometer with a test tube inserted in the bulb, as shown, and hermetically sealed therein. The shaded portion is full of alcohol, coloured red in

the product of the specific heat by the atomic weight, and is about 6·0. Thus ·05701 × 108 = 6·157.

order to make its motions in the stem more evident. The stem *s* should be about 30 cm. long, graduated clearly in millimeters. The instrument ought to be so constructed that the thread of liquid should advance through a length of fully 30 millimeters for an increase in temperature of one degree centigrade. The bulb of the atometer is bedded, as shown, in cotton wool contained in any convenient beaker, or better still, a heavy tumbler. A small piece of cotton wool is passed down to the bottom of the test tube *t*, and one cubic centimeter of water accurately delivered into the previously dry tube from a measuring pipette, or dropping tube, fig. 22. The whole apparatus is left in a cool place until the thread of liquid in the stem becomes steady, *i.e.* until the instrument acquires the same temperature.

FIG. 21.

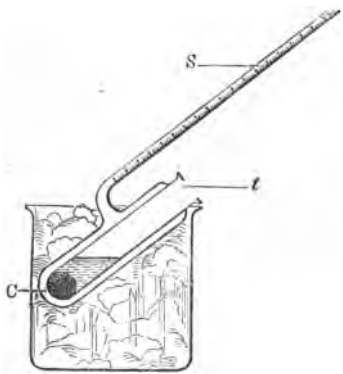
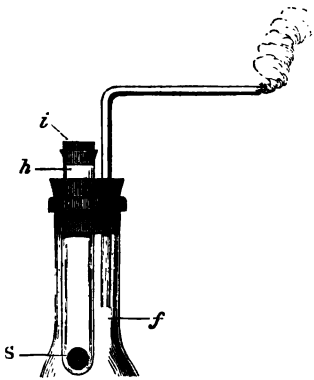


FIG. 22

Now take a piece of pure metallic silver weighing exactly 108 centigrams, and of such a shape that it can easily pass into the test tube *t* of the atometer. Place the centigram atom of silver in the test tube *h*, which passes rather

loosely through the cork of the flask *f*, fig. 23. The test tube should be closed by a small stopper of cork or vulcanite. Through the cork of the flask another tube passes which is open at both ends, and which gives exit to the current of steam produced when the water in the flask is boiled vigorously. The test tube and the contained silver are thus heated to the temperature of steam, *i.e.* 100° C. if the pressure be 760^{mm}. After ten minutes heating in the steam bath the metal will have acquired the desired temperature: then remove the tube *h* quickly, bring its mouth near to the mouth of the tube *t* of the atometer, withdraw the cork *i*, and so invert *h* that the lump of silver *s* may quickly drop into the water in *t*, where it parts with its heat. The little piece of cotton wool prevents the lump of silver from breaking the glass.

FIG. 23.



If the temperature, as indicated on the stem *s*, be noted just before the introduction of the silver, the thread of liquid will be seen to rise almost immediately after the silver has been dropped in, and will continue to rise until it reaches a maximum.

In an experiment made in this way the thread of liquid in the atometer rose from 10 to 39 (29 divisions) after the 108 c. grs. of silver had been introduced.

Now take 12 centigrams of pure magnesium in *lump*, not ribbon, place it in the tube *h*, and heat it to 100° C. in the same way as the silver.

While the magnesium is heating, pass a wire with a hook at the end into the tube of the atometer, and raise nearly to the mouth of *t* the piece of cotton wool which will carry with it the lump of silver. After the water has drained away from the latter, pick out the silver with a forceps and push the cotton back under the water, then remove the wire. At this time the liquid in the stem *s* will be still above the point from which it started in the experiment with silver, therefore remove the bulb *c* and blow upon it, or so cool it as to get the thread contracted to a lower point than we require; now replace in the wool, and allow the temperature to gradually rise, until the silver starting-point is reached. By this time the magnesium will have been heated to 100° C., and it is now to be plunged into *t*, as in the former experiment, and the rise in temperature noted.

In the particular experiment above referred to, the liquid expanded from 10 to only 25 (15 divisions) or to little more than *half* the extent that it did in the case of 108 c. grs. of silver.

The conclusion we draw from the results of such experiments is that 12 c. grs. of magnesium at 100° C., contain but half the quantity of heat that 108 c. grs. of silver do at the same temperature. We therefore infer that the weight of magnesium that would contain the same quantity of heat at 100° C. as 108 c. grs. of silver is 24 c. grs., and on repeating the experiment with this larger weight, and under the same

conditions as before, we get an expansion which is nearly equal to that caused by the silver. Now, according to our definition of the term equivalent,[1] silver cannot have a *less* atomic weight than 108; neither can it be *greater*, because the product of the equivalent into the specific heat of silver (see foot-note, page 57) gives the number 6·157, which accords, within narrow limits, with the *highest product* similarly obtained with any element whose atomic weight can be independently fixed by means of Avogadro's principle. Hence the weight of a solid element that contains at 100° C. the same quantity of heat as 108 parts of pure silver at 100° C. is the atomic weight of the body.

Therefore, according to Cannizzaro's modification of Dulong and Petit's law, 24 is the *atomic* as distinguished from the equivalent weight of magnesium.

It is right to add here that several exceptions are known to this and the preceding law, but these will be dealt with in the proper place.

[1] See page 26.

CHAPTER VII.

TABLE OF ATOMIC WEIGHTS—EXPERIMENTS WITH METALS AND NON-METALS.

THE annexed table contains a list of the principal chemical elements already recognised, and appended to each is the atomic weight which has been determined in most cases by appeal to the criteria employed in the course of our experiments. Opposite to the name of each element is placed a *symbol* by which it is indicated. The symbol for an element is in each case derived from either the English or Latin name of the particular body. Thus H is the symbol for Hydrogen, O for Oxygen, N for Nitrogen, Ag for Silver (from Argentum), Au for Gold (from Aurum).

When the same letter is the first of the name of more elements than one, *two* letters form the succeeding symbols; thus, B stands for Boron, Ba for Barium, Bi for Bismuth, Br for Bromine, and Be for Beryllium.

The symbol for an element when used alone always signifies *one atom* of the body: thus, if we take the centigram-atom as our unit, H signifies *one* centigram of Hydrogen; O, *sixteen* c. grs. of Oxygen; Ag, *one hundred and eight* c. grs. of Silver, and Mg, *twenty-four* c. grs. of Magnesium. The elements are arranged in alphabetical order in the table, but it is usual to

Name	Symbol	Atomic Weight
Aluminium	Al^{iv}	27.3
Antimony (*Stibium*)	Sb^{v}	122.0
ARSENIC	As^{v}	75.0
Barium	Ba''	137.0
Beryllium	Be''	9.2
Bismuth	Bi'''	210.0
BORON	B'''	11.0
BROMINE	Br'	80.0
Cadmium	Cd''	112.0
Calcium	Ca''	40.0
CARBON	C^{iv}	12.0
CHLORINE	Cl'	35.5
Chromium	Cr^{vi}	52.4
Cobalt	Co^{iv}	58.6
Copper (*Cuprum*)	Cu''	63.0
FLUORINE	F'	19.0
Gold (*Aurum*)	Au'''	196.2
HYDROGEN	H'	1.0
IODINE	I'	127.0
Iron (*Ferrum*)	Fe^{iv}	56.0
Lead (*Plumbum*)	Pb^{iv}	207.0
Lithium	Li'	7.0
Magnesium	Mg''	24.0
Manganese	Mn^{vi}	55.0
Mercury (*Hydrargyrum*)	Hg''	200.0
Nickel	Ni^{iv}	58.8
NITROGEN	N^{v}	14.0
OXYGEN	O''	16.0
PHOSPHORUS	P^{v}	31.0
Platinum	Pt^{iv}	194.5
Potassium (*Kalium*)	K'	39.1
SELENIUM	Se^{iv}	79.0
SILICON	Si^{iv}	28.0
Silver (*Argentum*)	Ag'	108.0
Sodium (*Natrium*)	Na'	23.0
Strontium	Sr''	87.2
SULPHUR	$S^{iv \text{ or } vi}$	32.0
TELLURIUM	Te^{iv}	128.0
Tin (*Stannum*)	Sn^{iv}	118.0
Zinc	Zn''	65.0

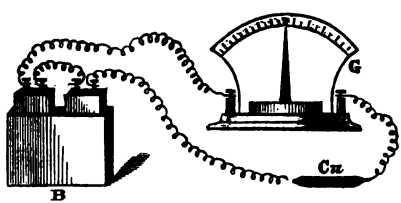
divide them in two great groups, of METALS and NON-METALS, respectively. The names of the former are printed in the table in strong Egyptian type, and those of the latter in capitals, in order to facilitate reference.

The most strongly marked members of each class admit of easy distinction.

Experiment 32.—Take a slip of copper, about ten centimeters long, and a roll of 'cane brimstone,' or sulphur, of the same length. Compare them and note:—

a. That the red-coloured copper exhibits that peculiar *lustre* termed metallic, while the yellow sulphur has a greasy lustre of a perfectly distinct kind.

FIG. 24.



b. That when one end of each specimen touches the surface of some boiling water, the fingers which grasp the other end quickly feel the heat *conducted* by the copper, while those holding the sulphur have not any sensation of warmth conveyed to them in the same time.

c. That the copper, *Cu*, fig. 24, when used to connect the terminal wires of the galvanic battery B with the galvanometer G in the circuit, *conducts* the electricity along it, as shown by the strong deflection of the needle. When the copper is removed,

and the wires connected by sulphur, the needle is *not* affected.

The metal copper is therefore distinguished from the non-metal sulphur—by the metallic *lustre*, and by conducting *heat* and *electricity* freely. These broad distinctions are sufficient for the present, but it must be stated that the members of each group cannot all be so sharply defined, and in some few cases it is by no means easy to determine whether in the free element—arsenic, for example—we have to deal with a metal or with a non-metal.

Experiment 33.—Again, take some crystals of 'blue vitriol,' or copper sulphate, and dissolve them in some hot water; now plunge into the solution two platinum slips attached to the terminal wires of a strong galvanic battery. Immerse for a minute or so, and observe that bubbles of gas separate from one of the plates; withdraw the slips, and note that a red deposit of metallic *copper* is obtained on the slip connected with the zinc end (the negative pole) of the battery. No deposit takes place at the other pole, but it was from this that bubbles of gas were separated, and this gas could be shown to be oxygen if collected and tested.

We learn, then, that when a compound of copper with a body which certainly contains oxygen is electrolysed, the *metal* makes its appearance at the *negative pole, i.e.*, that connected with the zinc end of the battery. The reason commonly assigned for this selection of the negative pole by the metal is, that the latter *being electro-positive* is most strongly attracted by the unlike pole, while the non-metal, oxygen, being *electro-*

negative, makes its appearance at the unlike, in this case the positive pole. This is true, not only of the copper compound, but of other compounds of a metal with a non-metal, when subjected to electrolysis; thus while the metals are electro-positive elements, non-metals are electro-negative.

Experiment 34.—Make a fresh solution of copper sulphate and place it in a phial; suspend a clean strip of iron wire in the liquid by means of a string fastened to the cork of the bottle.[1] A deposit soon forms upon the iron, and if the bottle be shaken it falls to the bottom; when the iron is taken out of the liquid it is seen to be coated with copper, and the deposit in the bottle is metallic copper. This action goes on until all the copper has been separated from the solution by the iron, the latter metal dissolving in the liquid. Metallic iron therefore displaces copper from solution without the assistance of a battery.

Experiment 35.—Next dissolve a small quantity of the poisonous 'corrosive sublimate,' or mercuric chloride, in hot water in a test tube, and plunge into the liquid a clean strip of copper. The latter soon becomes coated with a greyish deposit, and if we remove the copper, wash it with water and rub it, a bright silvery surface is obtained due to the separation of the metal mercury, or quicksilver, from the solution by the copper—the latter metal dissolving.

Experiment 36.—Again, dissolve a few crystals of silver nitrate in some water in a small phial, and pour a few drops of pure liquid mercury, or quicksilver, into

[1] Or plunge a clean steel knife into the liquid.

the solution, and allow the latter to stand for a day or so. At the end of that time beautiful needle-like crystals of metallic silver will be seen in the liquid, separated out from the solution by the mercury.

We thus learn that the metals are not equally electro-positive, thus iron being more electro-positive than copper displaced the latter from the solution; for a similar reason copper displaced mercury, and mercury the silver.

Experiment 36*b*.—The displacement of silver by magnesium already effected in Experiment 14, is another case in point, and the well-known 'lead tree' is a further illustration. In order to prepare the latter, dissolve about twenty grams of 'sugar of lead,' or lead acetate, in half a liter of water and place the solution in a flask of colourless glass. Secure a piece of clean zinc to a string and suspend the metal in the solution as shown (fig. 25). The metallic lead separates from the solution after some hours in beautiful plates or leaves, while the zinc slowly dissolves.

FIG 25.

From the results of experiments of the kind just described, we can draw up the following table of fourteen metallic elements arranged in electro-chemical order. Each metal is electro-positive to those above, and electro-negative to those below it in the list.

Electro-negative.	
Gold.	Lead.
Platinum.	Iron.
Silver.	Zinc.
Mercury.	Magnesium.
Copper.	Calcium.
Bismuth.	Sodium.
Tin.	Potassium.
	Electro-positive.

This order is subject to some variation with the nature of the liquid in which the experiments are made.

We now return to the symbols of the elements, and have to inquire to what uses they are put in expressing chemical changes.

With the symbols we can build up the 'formula,' of any definite chemical compound, and such an expression informs us of what kinds of matter the body is composed, and in what proportions the several constituents are present. Thus the formula NaCl expresses the composition of common salt, H_2O that of water, and $AgNO_3$ that of silver nitrate.

If we desire to find the formula by which the composition of common salt is to be expressed, we have to ascertain in the first instance of what elementary forms of matter it consists. With the aid of the methods of *qualitative analysis* we can prove that it consists of the two elements, sodium and chlorine. Our next step is to find the proportion of each element present, and this is accomplished by

the methods of *quantitative analysis*, and the results are stated in percentages.

100 parts of common salt afforded on analysis :—

Chlorine	60·62
Sodium	39·38
	100·00

These are facts, quite apart from any hypothesis; but in order to find the relative number of atoms of each element present in the compound, we divide the percentage of each constituent by its atomic weight, thus—

$$\frac{60{\cdot}62}{35{\cdot}5^{*}}=1{\cdot}7 \quad \text{and} \quad \frac{39{\cdot}38}{23^{\dagger}}=1{\cdot}7$$

Hence there is an equal number of atoms of each element in the compound, and the ratio of Na to Cl is 1 : 1. The formula of the body is, therefore—

1Na : 1Cl, or, more simply, NaCl,

for each symbol represents one atom of the element, and the approximation of the symbols without any sign between indicates that the definite compound, called common salt, is the product of the chemical union of the two elements sodium and chlorine. The chemical name of this compound is *sodium chloride.*

Again, 100 parts of water afforded on analysis—

Hydrogen . . .	11·11 ÷ 1 = 11·11 or 2.
Oxygen . . .	88·89 ÷ 16 = 5·55 or 1.
	100·00

* The atomic weight of chlorine.

† The atomic weight of sodium.

or, dividing by the lowest term, 2 atoms of hydrogen to 1 atom of oxygen, and this is expressed by the formula –

$$H_2O;$$

H_2 in this formula indicates two atoms of hydrogen. The chemical name of water is hydrogen monoxide.

Finally, 100 parts of silver nitrate afforded on analysis—

Silver	. .	63·52÷108=	·5881 or 1.
Nitrogen	. .	8·23÷ 14=	·5878 „ 1.
Oxygen	. .	28·25÷ 16=	1·7656 „ 3.
		100.00	

The quotients, ·5881 and ·5878, are so nearly equal that we may fairly set down the slight difference between them (·0003) to unavoidable errors of experiment; it is therefore a matter of indifference which term we employ to divide 1·7656. In either case the quotient is as nearly as possible 3. Hence while we have the same number of atoms of silver and nitrogen in the compound, we have 3 times the number of atoms of oxygen, and these atomic ratios are expressed by the formula—

$$Ag\,NO_3.$$

It often happens that we are given only the chemical formula of a body, and are required to find what its percentage composition must be. The solution of this problem is exceedingly simple, and is always effected by the method we shall now illustrate in the case of silver nitrate.

The first step is to find the *molecular weight* of the

body, *i.e.* the sum of the atomic weights of its constituents—thus:—

Ag	=108.
N	= 14.
O_3 (16 × 3) . .	= 48.
Weight of molecule .	=170.

Three sums in simple proportion then obtain the desired information.

170 : 100. :. 108 : 63·52	the percentage of	Ag.
170 : 100. :. 14 : 8·23	„	„	N.
170 : 100. :. 48 : 28·25	„	„	O.
	100·00		

The symbol $AgNO_3$ is called an *empirical* formula, because it expresses only the atomic ratios of the constituents, and does not convey any idea as to the way in which the elements are grouped within the molecule. If however we write silver nitrate thus,

$$Ag-O-NO_2,$$

we seek to convey the idea that the atom of silver is united by means of one oxygen atom to an oxygenated group, NO_2, and this is termed a *rational* formula. We shall presently meet with many such expressions.

If we examine lists of chemical formulæ, we can easily select a number of examples, such as the following :—

Formulæ.	Names.
1. HCl . .	Hydrogen Chloride.
1. HF . .	Hydrogen Fluoride.
2. H_2O . .	Hydrogen Monoxide.

Formulæ.	Names.
3. $AuCl_3$ . .	Gold Trichloride.
4. CCl_4 . .	Carbon Tetrachloride.
5. PCl_5 . .	Phosphorus Pentachloride.
6. MnF_6 . .	Manganese Hexafluoride.

All these compounds are *binary* compounds, or those containing only two kinds of matter; when three distinct elements unite, they form a *ternary* compound, as silver nitrate, $AgNO_3$. It is to be noted that the termination of all the above names is the syllable *ide*, and this occurs only in the names of *binary* compounds. Again, the symbol written to the left hand in each formula is that of the *most electro-positive constituent*, and this is also a general rule, though there are some exceptions to it. Lastly, the number of atoms of the electro-negative constituent in the molecule is indicated by the prefixes mono-, di-, tri-, tetra-, penta-, and hexa-.

But the consideration of these formulæ leads us another step forward, for we perceive that the elements H and Cl, as well as H and F, combine atom for atom (and as a matter of fact, in no other proportion), and are therefore said to be equal in chemical power. But a single atom of oxygen can attract and attach to itself *two*, but not more than two, atoms of hydrogen, as in water. Again, one atom of the metal gold can enchain, as it were, three, but not more than three, atoms of chlorine, as in gold trichloride. Similarly, one atom of carbon can fix the maximum number of four atoms of chlorine, as in carbon tetrachloride; the single phosphorus atom, five of chlorine, as in the penta-

chloride ; and the manganese atom, six of the element fluorine.

We thus learn that the atoms of the elements differ widely in chemical power. The *atom* of manganese resembles in this respect an open chain of six links, each one of which can attract and hold strongly one atom of the element fluorine ; phosphorus, a five link chain ; carbon, one of four links ; gold, one of three ; oxygen, one of two ; while the hydrogen, chlorine, and fluorine atoms are represented by single links.

We can thus divide all the known elements into those whose atoms are

1	link, or	Monad,	like	Hydrogen.
2	„	Diad	„	Oxygen.
3	„	Triad	„	Gold.
4	„	Tetrad	„	Carbon.
5	„	Pentad	„	Phosphorus.
6	„	Hexad	„	Manganese.

This hydrogen or chlorine fixing power of an element is often spoken of as the 'atomicity,' 'quantivalence,' or 'valence,' of its chemical atom, and is thus indicated in the symbols by the marks shown :—H′, O″, Au‴, C^{iv}, P^{v}, Mn^{vi}.[1]

But the atom of an element does not always act with its full chemical effect : thus nitrogen acts as a pentad in sal ammoniac, NH_4Cl, as a triad in ammonia, NH_3, and as a monad in nitrous oxide, N_2O, or laughing gas. Returning to our simile of the chain,

[1] The atomicity of each element is marked in the Table of Atomic Weights.

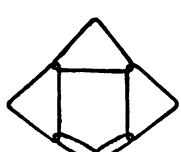
we say that the five link nitrogen atom may also act with but three links or one, the other links (*i.e.* centres of attraction, 'bonds,' 'equivalents,' or 'atomicities') becoming latent or inactive *in pairs*, owing to mutual satisfaction. If we regard the atom of nitrogen as a chain of five equivalents or links, we can easily illustrate the suppression of links in pairs.

Let the following diagram represent the nitrogen atom, acting as a *pentad*, by an open chain of five links, each one having but a single *free* point of attachment, *i.e.*, at a bend or angle; the chain should therefore consist of oval and triangular links.

FIG. 26.

If we close the chain by connecting the oval links, thus—

FIG. 27.

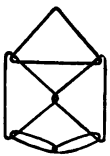


three points of attachment are still free, and we have a representation of the atom of nitrogen acting as an apparent *triad*.

The next diagram represents the monad condition of the nitrogen chain, in which but one bend remains free for attachment.

The disappearance of the points of attachment in pairs is thus seen to be a mechanical necessity in the case of the links of the chain.

FIG. 28.



A triad element, such as gold, would be represented as a chain of three links —one triangular and two oval, and this chain when closed would represent a seemingly monad gold atom, thus—

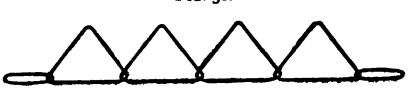
FIG. 29.

We are acquainted with a number of compounds, in which the gold atom acts as a monad.

An element which is never more than a monad, such as hydrogen, is best represented as a single *circular* link, as it has but a single centre of attraction.

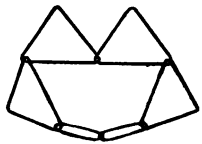
In this way we can symbolise the elements of uneven atomicity, or *perissads*. The atoms of elements of even atomicity, or *artiads*, may be represented in a similar way. Thus the manganese atom acting as a hexad—

FIG. 30.



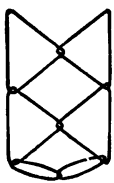
as a tetrad—

FIG. 31.



as a diad—

FIG. 32



The element carbon is a good example of a tetrad atom, and may be represented by a chain of two triangular and two oval links ; the closed chain corresponds to the carbon atom acting as a diad.

An element which is always diad can be best represented by a chain of two *oval* links, as in the next figure, in this we represent the composition of the molecule of water, which, as we have already seen, contains one atom of oxygen in union with two atoms of hydrogen.

FIG. 33.

The circular links are atoms of hydrogen, while the pair of oval links represent the atom of oxygen.[1]

Such representations of monad, diad, triad, &c., elements may be easily made in a short time by cutting some stout copper wire into equal lengths of about 10 centimeters, and bending each into one or other of the forms of link given above. The links can then be permanently coupled up into chains so as to represent atoms; and the latter can be employed in illustrating chemical combinations in the way already pointed out.

In using these aids to study, the beginner must carefully avoid regarding them as representations of atomic structure, or, in fact, as other than mere artificial aids.

The student will do well to attach the 'atomicity' marks, as in the table, to all chemical symbols, as he will thus become soon familiar with the replacing and combining values of the atoms.

The symbols as written are evidently capable of use in the explanation of chemical changes, and the latter are in fact represented by *chemical equations*. Thus the equation—

$$2H' + O'' * = H'_2O''.$$

is intended to represent that two atoms of H and one

[1] The free molecules of the elements containing two atoms may obviously be represented by two systems of links, so united that every link of each chain is fully engaged.

* The *plus* sign + signifies 'added to,' or 'when made to act chemically upon.' The sign of equality =, stands for the word 'produce.'

of O, when brought together under the proper conditions, unite, and produce the compound water. The number of atoms of each kind of matter on one side of an equation must evidently be equal to that on the other, hence we say—*the weights of the product or products, of a given change, must be equal to the sum of the weights of the bodies taking part in the reaction.*

Again—

$$H'_2O'' = O'' + 2H'$$

indicates that the compound water has suffered decomposition, and that the products are one atom of O and two atoms of H. In other words, 18 c. grs. of water can afford on decomposition 2 c. grs. of H, and 16 c. grs. of O.

These examples are sufficient for the present, but many others will be given as we proceed. It must be added, however, that the student should not look upon every equation that complies with the above rule as being necessarily a correct one; it must not only equate, but represent the facts as accurately as possible: therefore the quantitative experimental test is the only true one of the accuracy of an equation.

NOTE FOR THE STUDENT.—This chapter and the next one should be referred to from time to time as the student proceeds on his course and acquires further knowledge of chemical phenomena.

CHAPTER VIII.

EXPERIMENTS WITH ACIDS, ALKALIES, AND SALTS.

Experiment 37.—Take some common hydrochloric, or 'muriatic' acid, dilute it with about twenty times its volume of water. Note that the liquid has a *sour taste*,[1] and that a piece of *blue litmus* paper is reddened when dipped into the liquid. Then add a small quantity of common 'bread soda,' and note that brisk effervescence takes place, much gas being evolved.

Experiment 38.—Take some *aqua fortis*, or nitric acid, and dilute it to the same extent as the former acid with water. Note that it also tastes sour, reddens litmus, and causes effervescence when bread soda is added to it.

Experiment 39.—Again, take some 'oil of vitriol,' or sulphuric acid, and dilute it with twenty times its bulk of water, adding the strong acid *to the water* drop by drop, and stirring with a glass rod. This solution is also sour, reddens litmus, and sets up effervescence when bread soda is added to it.

If we extended our experiments to all known acids which are soluble in, or can be easily mixed with, water, we should find them to possess in a greater or less degree the characters detected in the

[1] Like vinegar, which contains a body called acetic acid. All strong acids must be cautiously handled, as they are generally corrosive.

three acids tested. The formulæ of these acids are given below—

HCl	Hydrochloric acid.
HNO_3 . . .	Nitric acid.
H_2SO_4 . . .	Sulphuric acid.

Experiment 40.—Dissolve a piece of 'caustic soda,' or sodium hydrate, the size of a grain of barley, in nearly a test tube full of water, and mix the liquid thoroughly by closing the mouth of the tube with a thumb and shaking. When the solid has quite dissolved, note that the solution has a somewhat earthy taste; that it does *not* redden blue litmus paper, but *restores* the colour of the paper already reddened by an acid. The addition of a diluted acid does not cause any effervescence, or but a very few bubbles of gas appear.

Experiment 41.—Dissolve in a similar way a small piece of 'caustic potash,' or potassium hydrate, and test it in the same way.

The two bodies just experimented with are often called 'the fixed alkalies,' or 'bases,' the latter term being generally applied to bodies which possess characters *opposed* to those of an acid. The formulæ of the two bases are the following—

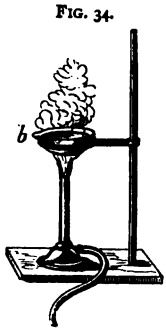
$NaOH$.	Sodium hydrate, or caustic soda.
KOH .	Potassium hydrate, or caustic potash.

Opposed as acids and bases are in characters they can easily *neutralise* one another.

Experiment 42.—Take a piece of caustic soda

about the size of a bean, dissolve it in about 30 c. cs. of water. Pour the liquid into an evaporating basin, *b*, fig. 34, and throw into the liquid a strip of blue litmus paper. Now add, drop by drop, colourless hydrochloric acid, stirring the liquid in the basin after each addition until the litmus paper begins to assume a reddish colour. If we now taste the solution it has a *salt taste*, the action of it on litmus paper is neither acid nor alkaline, and the solution is said to be *neutral*; the acid character of the hydrochloric acid has been exactly counter-balanced by the alkaline property of the caustic soda, and a *salt* is the product. If now we place the basin on the ring of the retort stand and apply heat, as shown in fig. 34, the solution soon boils, and the water is gradually converted into steam or vapour, and is driven off, or *evaporated*. When the liquid has been thus reduced to a very small bulk, little granular crystals separate. Pour off the liquid and allow the crystals to dry. They will then be found to possess the familiar characters of *common salt*. Therefore that body is produced when we neutralise hydrochloric acid by caustic soda. The formula of common salt is NaCl.

FIG. 34.



The following equation expresses the change :[1]—

[1] If 'bread soda' instead of caustic soda be treated with hydrochloric, or other soluble acid, a gas—carbon dioxide, or 'Carbonic acid'— is evolved, as in Experiments 37, 38, and 39,

$$\underbrace{Na'O''H'}_{\text{Sodium hydrate, or caustic soda.}} + \underbrace{H'Cl'}_{\text{Hydrochloric acid.}} = \underbrace{Na'Cl'}_{\text{Sodium chloride, or common salt.}} + \underbrace{H'_2O''.}_{\text{Water.}}$$

In this case the H and Na change places, and we may regard this as equivalent to a replacement of the atom of H in HCl by the atom of monad Na.

Experiment 43.—A precisely similar experiment may be made with caustic potash and nitric acid. In this case the salt crystallised from the neutral solution is common *nitre.*

$$\underbrace{K'O''H}_{\text{Potassium hydrate, or caustic potash.}} + \underbrace{H'NO_3}_{\text{Nitric acid.}} = \underbrace{K'NO_3}_{\text{Potassium nitrate, or 'nitre.'}} + \underbrace{H_2O.}_{\text{Water.}}$$

Experiment 44.—Again, take some caustic potash and neutralise it with sulphuric acid, previously diluted with five or six times its volume of water. Evaporate the solution and hard crystals of the salt potassium sulphate, K_2SO_4, separate out: in this case—

$$\underbrace{2(K'OH)}_{\text{Potassium hydrate.}} + \underbrace{H'_2SO_4}_{\text{Sulphuric acid.}} = \underbrace{K'_2SO_4}_{\text{Potassium sulphate.}} + \underbrace{2H_2O.}_{\text{Water.}}$$

This equation states the fact that one molecule of sulphuric acid requires for neutralisation twice as

otherwise the same products are obtained. Thus, in the case of hydrochloric acid:

$$\underbrace{NaHCO_3}_{\text{Bread soda.}} + \underbrace{HCl}_{\text{Hydrochloric acid.}} = \underbrace{NaCl}_{\text{Common salt,}} + \underbrace{H_2O}_{\text{Water.}} + \underbrace{CO_2}_{\text{Carbonic acid gas}}$$

much (*i.e.*, two molecules) caustic potash as the molecule of nitric acid did. The reason for this is that the molecule of sulphuric acid contains *two* atoms of H, and, as we have already seen, each atom of H requires an atom of monad metal such as K to replace it ∴ two molecules of KOH were required, because the necessary number of atoms of K could not be obtained in any less quantity.

But, as we shall find later on, it is possible to displace only half the hydrogen by K in such an acid as sulphuric and to form an *acid salt*, $KHSO_4$, or acid potassium sulphate—a body which still contains hydrogen capable of replacement by a metal. The compound, K_2SO_4, is the neutral or 'normal' salt.[1]

Although it is not desirable to go much further in this direction at present, we can evidently draw the following conclusions from the foregoing experiments and statements.

1st. That acids do not necessarily contain oxygen, else the undoubted acid HCl could not belong to that class of bodies.

2nd. That the acids used contain H replaceable by a metal, with the production of a salt. This is true of *all* acids.

3rd. That all acids do not contain the same number of atoms of replaceable H within their molecules.

Those acids containing *one* atom of replaceable H,

[1] A group of bodies termed 'double salts' is known; common *alum* is a good example of such a salt, for in it we have united two normal salts, viz., potassium sulphate and aluminium sulphate. The formula of anhydrous alum may be thus written—$K_2SO_4,Al_2(SO_4)_3$.

or 'basic hydrogen,' as it is sometimes called, are termed *monobasic* acids, and those containing two atoms are termed *dibasic* acids. *Tribasic* and *tetrabasic* acids, likewise exist, containing respectively three and four atoms of basic hydrogen. Generally, monobasic acids are the only members of the class which do not form acid salts.

It may be added that we can recognise in all salts an electro-positive constituent—the metal or metal-like body—and an electro-negative constituent, or *acid radicle.* When the latter is an element, such as chlorine in NaCl, it is a *simple radicle*; but if it consists of a group of two or more elements, such as NO_3 in KNO_3, or SO_4 in K_2SO_4, it is called a *compound radicle.*

CHAPTER IX.

FURTHER EXPERIMENTS WITH HYDROGEN.

HYDROGEN. *Symbol* H′=1. 1 *Vol*[1] *weighs* 1 *c.gr. Molecular weight* =2.—This element, which was discovered by Cavendish in 1766, has already been experimented with, and we have found it to be a colourless, inodorous, and extremely light gas, which can burn in air, and then affords water as the sole product of its combustion. We have also proved that it forms $\frac{1}{9}$th of water by weight.

Water is the chief terrestrial storehouse of hydrogen, for it rarely occurs in the free state upon the earth, save in certain gases which issue from active volcanoes. It is a constituent of animal and vegetable tissues, and of *all true acids.*

The hydrogen can be liberated from *water*, as we have already seen (Experiment 22), by electrolysis, in which case the compound is resolved into its constituents

$$H_2O=2H+O.$$

Experiment 45.—Hydrogen is also separated from water when we project a pellet of the metal sodium, the size of a pea, on some cold water contained in a dish. The water is decomposed with a hissing noise as the globule of metal rolls about on the surface,

[1] For meaning of this term see page 102.

and if a flame be brought near to it, the hydrogen gas evolved is ignited, and burns with a yellow flame, until the sodium disappears. If we do not ignite the gas, the metal also disappears, dissolving in the water.

$$\underbrace{Na}_{\text{Sodium.}} + \underbrace{H_2O}_{\text{Water.}} = \underbrace{NaOH}_{\text{Caustic soda or sodium hydrate.}} + H$$

The caustic soda can be recognised in the water by its property of turning reddened litmus paper blue. See Experiment 40.

In this case the monad metal replaces only *one* atom of H in the water molecule, and a *metallic hydrate* or *hydroxide* is formed, *i.e.* water in which the hydrogen *rôle* is played in part by the Na.[1]

H′O″H′	Water.
Na′O″H′	Sodium hydrate.

Experiment 46.—If we substitute a pellet of the metal potassium for the sodium in the last experiment, the metal also dissolves and produces potassium hydrate or hydroxide.

$$\underbrace{K'}_{\text{Potassium.}} + \underbrace{H_2O''}_{\text{Water.}} = \underbrace{K'O''H'}_{\text{Caustic potash or potassium hydrate.}} + \underbrace{H}_{\text{Hydrogen.}}$$

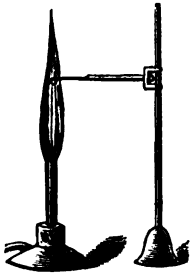
But in this case the temperature of the evolved

[1] It is possible to displace the second atom of H in water by another atom of Na, but not in presence of much free water as in the experiment.

hydrogen is raised by the heat of chemical action to such a point that it takes fire in the air, and burns with a reddish violet flame: thus the metal seems to set fire to the water!

Experiment 47.—As we have already seen, the colour of the pure hydrogen flame is a very faint blue, but the yellow flame observed in Experiment 45 is due to the presence of a little sodium vapour, which communicates to the flame the characteristic tint observed. Any compound of sodium, such as common salt, NaCl, will also communicate a strong yellow tint to an otherwise colourless spirit or gas flame, if we introduce a little of the solid supported on a loop of platinum wire, as in fig. 35. This is therefore a *flame test* for sodium.

FIG. 35.

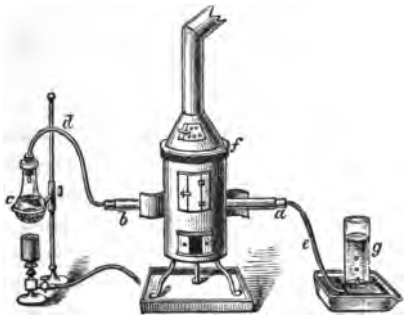


Similarly potassium and its compounds communicate an equally characteristic reddish violet colour to flame.

Experiment 48.—Hydrogen can also be displaced from water by the action of red hot iron on steam. Take an old gun barrel, fig. 36, and fill it to within a few centimeters of each end with bright iron turnings or borings; then pass the tube through the little charcoal furnace *f* (or heat the tube by a row of Bunsen gas burners), and connect one end *b* by means of a cork and leaden tube *d* with the flask *c*, in which some water can be made to boil and afford a current of steam. Attach a cork *a* and gas delivery tube *e* of lead or glass to the other end, and let *e* dip under

the surface of the water in the pnuematic trough *g*. When the iron tube has been heated to full redness, boil

FIG. 36.



the water in *c* and pass in the steam. Gas will issue from the delivery tube, but most of it is air at first, and may be allowed to escape; a few tubes full are then collected, and may be tested as in Experiment 19. The following equation represents the change.

$$\underbrace{3Fe}_{\text{Iron.}} + \underbrace{4H_2O}_{\text{Water.}} = \underbrace{Fe_3O_4}_{\text{Magnetic oxide of iron.}} + 8H$$

In this case a metallic hydrate is not formed, but a *metallic oxide*[1] is produced, and found as a layer on the surface of the iron turnings. It has been found, by careful experiment, that three atoms of the iron, or 168 c. grs. (56×3), liberate eight atoms, *i.e.* 8 c. grs. of H by weight, and these data enable us to calculate the weight of H which can be evolved by any given

[1] For an application of this method to the protection of iron surfaces, see under IRON, Part III. p. 174.

weight of iron (say 10 centigrams) from an excess of steam. Thus in the case supposed :—

$$168 : 10 :: 8 : x \quad (x = 0.476 \text{ c. grs.}—\textit{Ans.}).$$

Hydrogen can also be displaced from sulphuric acid by the action of magnesium, as in Experiment 17, and by iron or zinc, Experiment 19. Zinc is the metal most commonly used.

Experiment 49.—Fit up the apparatus as in Experiment 19. Having introduced the zinc, and filled the bottle one-third with water, replace the cork, and pour two or three cubic centimeters of acid down the thistle funnel. Hydrogen is soon evolved as before, and gas bubbles through the water in the trough. Allow a volume of gas, judged to be about equal to twice the capacity of the bottle, to escape, and then collect in jars for experiment, as before.

$$\underbrace{Zn''}_{\text{Zinc.}} + H'_2SO_4 = \underbrace{Zn''SO_4}_{\text{Zinc sulphate.}} + 2H$$

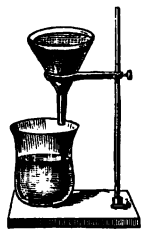
In this case, the single atom of diad zinc displaces the two atoms of monad H from the acid, and forms zinc sulphate which remains in solution.

Experiment 50.—When all evolution of gas has ceased, remove the cork, and pour the contents of the bottle on a filter, supported by a funnel as in fig. 37,[1] any undissolved zinc, and particles of carbon,

[1] A filter is thus made. Cut a circular piece of white bibulous paper about a decimeter in diameter, double this so as to form a semicircle, and double again so as to form a quadrant, now convert this into a paper cone with *three* folds of the paper on one side, and one fold or thickness on the other. Place this, point downwards, in the funnel, as shown, and moisten with a little water.

lead, and other impurities not dissolved by the diluted acid are left behind on the filter, while a clear liquid passes through, and the latter when evaporated (as in Experiment 42), until a pellicle or crust begins to form on the surface of the solution, deposits fine needle-shaped crystals of the salt, zinc sulphate—a body having the composition $ZnSO_4,7H_2O$. The water included in the formula is termed 'water of crystallisation,' as its presence is essential to the existence of the crystals as such, but not to that of the compound zinc sulphate, as almost every trace of the water can be driven off in the form of steam when the crystals are carefully heated to a temperature of 260° C.

FIG. 37.



Experiment 51.—After repeating former experiments take a gas jar standing over water in the trough, half fill with hydrogen and the remainder with air, remove and quickly apply a flame, and an explosion takes place. If pure oxygen be used instead of atmospheric air, the tube should be two-thirds filled with hydrogen and the rest with oxygen. In the latter case the explosion is more violent, and it is well to wrap the jar in cloth before applying the flame.

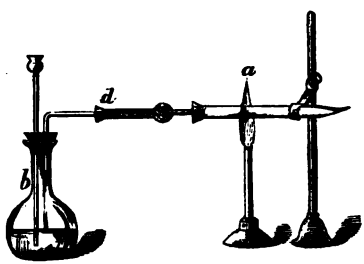
Hydrogen gas, when inhaled into the lungs of animals, causes death by excluding air.

Hydrogen forms two compounds with oxygen—one, water, H_2O, whose composition we have already determined; and a body termed peroxide of hydrogen,

or oxygenated water, H_2O_2, whose preparation and properties will be referred to later on.

Experiment 52.—The ease with which hydrogen combines with oxygen renders it a useful 'reducing' or *deoxidising* agent, especially when heated. Take a tube, about 1 centimeter in diameter, and 20 centimeters long. Place midway in it, at *a*, fig. 38, a small quantity of black oxide of copper, CuO, and connect the tube as shown with the hydrogen bottle *b*, taking care to

FIG. 38.



interpose the drying tube *d* filled with calcium chloride, so as to remove moisture from the gas. Generate hydrogen as usual and keep up a steady current through the apparatus. When all air has been expelled, but not till then, apply heat to the tube so as to raise the temperature of the copper oxide at *a*; the latter soon begins to glow and steam issues freely from the end of the tube. The lamp may be removed, and when the glowing ceases the tube is seen to contain a red body, easily identified as metallic copper. The change is expressed by the equation—

$$\underbrace{Cu''O''}_{\text{Copper oxide.}} + 2H = \underbrace{Cu}_{\text{Metallic copper.}} + H_2O.$$

This reaction was employed by MM. Dumas and Boussingault in order to determine with extreme precision the composition of water by weight. They heated to redness a carefully weighed quantity of pure copper oxide in a current of perfectly pure and dry hydrogen gas, and collected and weighed the water produced.[1] In one of their experiments the cupric oxide lost 59·789 grams of oxygen, and the water produced weighed 67,282 grams. The composition of this weight of water is, therefore—

Hydrogen	7·493
Oxygen	59·789
	67·282

Calculate the *percentage* composition of water and deduce the formula from these data by the method given at page 70.

Experiment 53.—Substitute for the copper oxide in Experiment 52 some iron rust in fine powder. The red rust—consisting chiefly of a sesquioxide[2] of iron—then becomes greyish black when heated to redness in hydrogen, and water is produced. The black

[1] We have already (Experiment 21) made a similar experiment by another method, *viz.*, by the combination in air of a weighed quantity of hydrogen gas, the weight of water produced being collected and weighed.

[2] From *sesqui*—one and a half, for the ratio of Fe to O is 1 to $1\frac{1}{2}$; but since an atom is indivisible, the simplest expression for the oxide is Fe_2O_3.

body left in the tube chiefly consists of metallic iron in a very fine state of division, in which condition the metal easily takes fire, if the warm powder be poured out through the air.[1] In this condition the metal is said to be *pyrophoric.*

$$Fe_2O_3 + 6H = 2Fe + 3H_2O.$$

Thus prepared from pure oxide, the metal constitutes the *Fer réduit*, or *Ferrum redactum* of the British Pharmacopœia.

Hydrogen gas is absorbed by water in very small proportions, 100 cubic centimeters of the latter dissolve only 1·93 c. cs. But some solid metals absorb hydrogen, notably the metals platinum[2] and palladium. The latter takes up no less than 370 volumes of the gas at ordinary temperatures.

Hydrogen gas has been recently condensed by M. Pictet of Geneva to a liquid, exhibiting steel-blue *metallic* lustre, under the enormous pressure of 650 atmospheres, and at a temperature of 140° C. below zero: the gas is, therefore, to be regarded as the vapour of a highly volatile *metal.*

[1] The same weight of iron in the form of wire would but slowly rust or oxidise when exposed to the air; the above experiment therefore well illustrates the effect of a fine state of division in determining rapid chemical changes.

[2] For a description of the Döbereiner lamp see Platinum, Part III. Experiment 419.

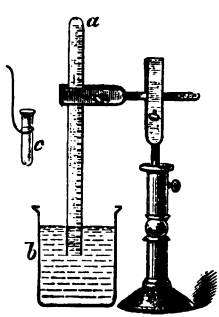
CHAPTER X.

EXPERIMENTAL DETERMINATION OF THE VOLUME OCCUPIED BY ONE CENTIGRAM OF HYDROGEN.

WE have already learned from Experiment 18 that 1 centigram weight of hydrogen gas is evolved from acidulated water during the solution of 12·2 c. grs. of pure metallic magnesium; we, therefore, know how to get our unit weight of hydrogen. In the experiment cited we allowed the gas to escape: we shall now collect the gas and measure it.

Experiment 54.—Obtain a tube about 40 c. ms. long and 2 c. ms. internal diameter, graduated into 130 cubic centimeter divisions, *a*, fig. 39. Dilute 50 c. cs. of oil of vitriol with about a liter of water in a jug, and throw into the liquid a few scraps of metallic zinc. Hydrogen will be developed and the liquid will have nearly or quite saturated itself with the gas in a few minutes. Next pour some of the diluted acid into a tall narrow beaker *b*, and, having filled the graduated tube

FIG. 39.



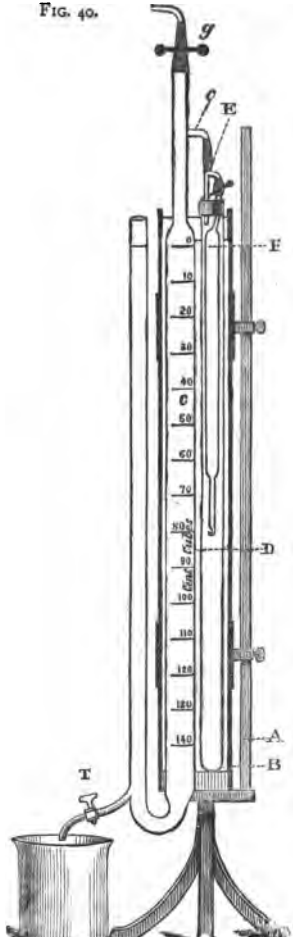
completely with the same liquid, invert it in the acid in the beaker and support it as shown.

Now weigh out 12·2 c. grs. of pure and clean metallic magnesium—the weight of the metal that we know will liberate 1 c. gr. of hydrogen—and place it in the bottom of a narrow test tube, *c*, to the middle of which a wire is attached to serve as a handle. The tube is then filled with water and plunged under the surface of the acid in *b*, and the upturned mouth of the test tube *rapidly* brought under the mouth of the graduated tube, and even passed up into the latter. Very soon the acid liquid displaces the water in the test tube and the metal is attacked; the hydrogen gas evolved passes into the inverted tube and there collects. When the last trace of magnesium disappears the action is at an end, and we have confined in the tube the volume of pure hydrogen gas that weighs 1 centigram. Now depress the tube in the acidulated water until the liquid within and without the tube stands at the same level, and read off the volume of the enclosed gas. Immediately afterwards read the *temperature* as indicated by a thermometer in the neighbourhood of the apparatus, and the *pressure* as indicated by a barometer.

A more precise experiment can be made with the apparatus, fig. 40. The stand A supports a tall glass cylinder, B. Through the large india-rubber cork which closes the lower opening of the cylinder the U tube *c* is passed, great care being taken to avoid breaking the small T connector *c*. The outer limb of the U tube is provided with a glass tap T. The limb within the tall glass cylinder is sufficiently wide

to contain 150 cubic centimeters in the expanded portion, which, in our apparatus, measures sixty centimeters in length. The graduation cannot be conveniently carried beyond fifths of a cubic centimeter. At the point shown an india-rubber tube *g* is attached, which can be closed at will either by a good clip or by a stopper of glass rod. The glass side tube *c* serves to connect the measuring apparatus, filled to 0 with water, with the generating vessel D, which is a long and wide glass tube placed within the cylinder. The glass T tube E is connected by means of rubber tubing with *c*, while one limb passes through the india-rubber cork of D, and the other is connected by another

FIG. 40.



piece of rubber tubing with a fine tube of the long pipette F (of about 20 c.cs. capacity), which projects through the cork. This connection must be sufficiently long to admit of the clip being applied as shown.

The large glass cylinder B is filled with water, in order to maintain a steady temperature, the value of which can be known by means of a thermometer immersed in the water.

A determination is made with this apparatus in the following way:—Having disconnected the T tube E from *c* and removed the clip, the tube D is taken out of the water of the cylinder, the cork carrying the pipette, &c., withdrawn, and then 12·2 c. grs. of magnesium introduced into the tube D. Before replacing the cork the pipette F is filled with diluted sulphuric acid by suction at E, while the small glass tube opening on the under side of the cork is closed by a finger: the clip is then applied. The exterior of the pipette is now washed with a little water, and the cork, with the apparatus attached, is then replaced in position; the tube D again immersed in the water of the large cylinder, and the joint between E and *c* securely made. Before making the connection the water in the graduated tube should stand at the zero of the scale, but after securing the joint the pressure within the apparatus is usually greater than that without. As the air in the tube D cools down to the temperature of the surrounding water, contraction takes place; but should the water not return to the zero, equilibrium is at once restored by opening the fine india-rubber tube *g* for a few

seconds, and then closing in such a manner as to prevent any possible escape of gas.

The acid is brought in contact with the magnesium by removing the clip from the india-rubber tube connected with the pipette; the re-agent then falls upon the metal at the bottom of the tube D. Hydrogen is evolved and displaces water from *c*, the liquid being maintained at the same level in both limbs of the U tube by allowing the water displaced to run off by means of the tap T. When the evolution of gas has ceased, the water level is adjusted by means of the tap, and the volume of gas produced in the reaction then read off on the graduated tube; the temperature of the water in the cylinder B is then ascertained, as well as the height of the barometer at the time. From the data thus obtained, the volume of dry hydrogen at 0° C. and 760 mm. can be easily calculated.

A student obtained, as the result of an experiment made in the simple apparatus shown in fig. 39, 121 c. centimeters of pure but moist hydrogen, measured at 16° C. and 755 millimeters pressure, during the solution of 12·2 c. grs.[1] of magnesium in acidulated water.

So far for our experiment: we now have to find the volume this gas would occupy if dry and measured at 0° C. and 760 millimeters—the 'standard temperature and pressure' to which all gaseous volumes are corrected, for reasons that will presently appear.

The corrections are three in number—namely: for *tension of aqueous vapour*, for *pressure*, and for *tem-*

[1] The 2 milligrams in excess represent the known proportion of impurity in the sample of metal.

perature, and we shall deal with each in some detail in order to illustrate the method of solving such problems.

1. *Correction for tension of aqueous vapour.*[1]—We find from the annexed table of tensions for different temperatures that at 16° C. the pressure exerted by vapour of water =13·5 mm., that is to say, the pressure exerted by the aqueous vapour within the tube tended to balance the atmospheric pressure to the extent of a column of mercury of 13·5 millimeters in height; therefore the actual pressure under which we measured the confined gas was

$$755 - 13{\cdot}5 = 741{\cdot}5 \text{ millimeters of mercury.}$$

TENSIONS OF AQUEOUS VAPOUR.

Degrees Centigrade	Tensions in millimeters of mercury	Degrees Centigrade	Tensions in millimeters of mercury
0	4·60	19	16·34
5	6·53	20	17·39
10	9·16	30	31·54
11	9·79	40	54·90
12	10·45	50	91·90
13	11·16	60	148·70
14	11·90	70	233·00
15	12·69	80	354·60
16	13·53	90	525·40
17	14·42	100	760·00
18	15·35		

2. *Correction for pressure.*—We learned from Experiment 28 that when a confined mass of gas was

[1] The student must refer to a work on Physics for full details of corrections of volumes of gases.

compressed, its volume or bulk *diminished with increase of pressure*, and conversely, *increased in volume as the pressure diminished.* Thus, if the pressure on a given mass of gas be doubled, the volume is reduced to *one-half*, and if trebled, to *one-third*, and so on. When the original pressure is restored the gas returns to its original volume. If now we *reduce* the pressure to one-half, the volume of gas is *doubled*; if to one-third, the volume is *trebled*, and so on. These facts find expression in the law of Boyle or Mariotte: '*The volume which a gas occupies is inversely proportional to the pressure to which it is subjected.*' Now 741·5 mm. being a lower pressure than the standard 760 mm., our gas would occupy a less volume at the greater pressure; how much less we find thus—

$$760 : 741{\cdot}5 \therefore 121 : \varkappa \quad (\varkappa = 118{\cdot}5 \text{ c.cs.}).$$

3. *Correction for temperature.*—Experiment 28 also showed us that gases expand equally when heated, and contract when cooled. If we begin with a given volume of gas at the temperature of melting ice, *i.e.* 0° C., and measure the gas as we raise its temperature at a definite rate, we find that for each rise in temperature by 1° C. the gas expands $\frac{1}{273}$rd of its volume at 0° C. That is to say, 273 c.cs. at 0° C. expand to 274 c.cs. if the temperature be raised to 1° C.; or to 280 c.cs. if heated to 7° C.; or to 289 c.cs. if heated to 16° C.; the pressure throughout being constant. Similarly, 289 c. cs., cooled to 0° C. contract to 273 c. cs. Hence we can easily find the volume that 118·54 c.cs. of gas at 16° C. would occupy if cooled to 0° C.; thus—

$$289 : 273 \therefore 118{\cdot}5 : \varkappa \quad (\varkappa = 111{\cdot}9 \text{ c.cs.}).$$

The final result is that 1 centigram of pure dry hydrogen, when measured at 0° C. and 760 mm. pressure, occupies as nearly as possible 112 c.cs. As we have already adopted the centigram as our unit of weight, we may conveniently take the bulk of 1 c.gr. of hydrogen, measured under standard conditions, as our unit of volume, and call it briefly a *vol.* Thus when we speak of 1 *vol* of any gas, we mean 112 c.cs. of it measured at 0° C. and 760 mm.[1]

The *vol* as thus defined is a small and convenient quantity of a gas, which is well within the capacity of the ordinary measuring vessels used in laboratories; moreover it possesses the great advantage over the liter as a unit of gaseous volumes, that its weight in hydrogen is identical with the atomic weight of that body in centigrams; consequently a *vol* of any other elementary gas weighs the number of centigrams indicated by the atomic weight of the element. Thus—

Name of gas	Atomic weight	Weight in centigrams of 1 *vol* (at 0°C. and 760 mm.) or 112 c. cs.
Hydrogen . . .	1.0	1.0 c. gr.
Oxygen	16.0	16.0 ,,
Nitrogen . . .	14.0	14 0 ,,
Chlorine . . .	35.5	35.5 ,,

[1] A number of *vol* tubes may be prepared by cutting a good cylindrical glass tube 4.2 centimeters diameter into lengths of 7.8 centimeters, one end of each tube is then closed by a glass plate which is cemented on. Each tube or jar should hold 112 c. cs. of water. We have a number of these jars prepared and filled with different coloured wool, in order to illustrate the volume relations of elementary and compound gases.

Hence in order to find the weight of a given bulk of gas, for instance, of 900 c.cs. of hydrogen at standard temperature and pressure, it is merely necessary to proceed as under :—

$$112 : 900 \therefore 1 : x \quad (x = 8{\cdot}03 \text{ c.grs.}).$$

But if the gas were oxygen—

$$112 : 900 \therefore 16 : x \quad (x = 128{\cdot}57 \text{ c.grs.})$$

Generally— $$x = \frac{n \times \text{at. wt.}}{112}$$

Since the *vol* of hydrogen represents the semi-molecule of that element, the molecular weight being 2 as we have already seen (see page 52), the *vol* also represents the semi-molecule of any compound gas—water gas, for example—consequently the weight of one *vol* of a compound gas is *half* the molecular weight in centigrams. Thus—

Name of gas	Molecular Formula	Molecular weight	Weight in centigrams of one *vol* (at 0°C. and 760) *i.e.* 112 c. cs.
Hydrogen . .	H_2	2	1 c. gr.
Water gas . .	H_2O	18	9 ,,
Hydrochloric acid gas . . .	HCl	36.5	18.25 ,,
Ammonia . .	NH_3	17	8.5 ,,
Marsh gas . .	CH_4	16	8 ,,
Carbon dioxide .	CO_2	44	22 ,,
Carbon monoxide .	CO	28	14 ,,

The numbers in the fourth column are identical with the specific gravities of the gases referred to hydrogen as the standard. *In order to find the weight*

in centigrams of a given bulk of a compound gas—for instance, of 1200 c. cs. (=1·2 liters) of ammonia gas at standard temperature and pressure—we say—

$$112 : 1200 \therefore 8{\cdot}5 : \aleph \quad (\aleph = 91 \text{ c. grs.}).$$

If the gas were hydrochloric acid gas—

$$112 : 1200 \therefore 18{\cdot}25 : \aleph \quad (\aleph = 195{\cdot}5 \text{ c. grs.}).$$

Generally—

$$\aleph = \frac{n \times \text{sp. gr.}}{112}$$

when n = the number given in cubic centimeters of dry gas at 0° C. and 760 mm.

Instead of the *vol*, we may use the liter as our unit of volume. The weight of a liter of pure dry hydrogen at 0°C. and 760 mm. is ·08936 (this weight is called by Dr. Hofmann a *crith*). A liter of oxygen weighs 16 criths, of chlorine 35·5 criths, of nitrogen 14 criths, &c. A liter of water-gas weighs 9 criths, of ammonia 8·5 criths, of hydrochloric acid gas 18·25 criths, &c.

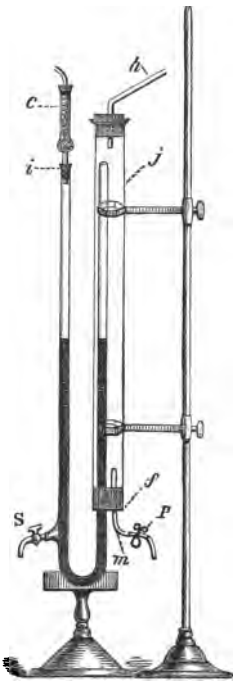
We have already learned from Experiment 29 that the specific gravity of the compound water gas is half its molecular weight, and the above table tells us the same thing for other compound gases. If then we have presented to us a gas of unknown composition, *we can determine its molecular weight* by first taking its specific gravity, as in Experiment 27, and that value, when doubled, should give the molecular weight of the compound. Thus, ammonia gas has the specific gravity 8·5, its molecular weight is therefore $8{\cdot}5 \times 2 = 17$.

Hydrochloric acid gas has the specific gravity 18·25; the molecular weight of the compound is therefore $18{\cdot}25 \times 2 = 36{\cdot}5$.

There are a few exceptions to this important rule, which will be noticed in the proper place.

Experiment 55.—Take a U tube of the form shown in fig. 41, with limbs 60 centimeters long. Let one limb be hermetically sealed at the top and the other open. A stopcock is provided near to the bend of the open limb. Now fill both limbs completely with mercury so as to expel all air, then insert the cork *i*, through which passes the end of a small tube open at both ends, and filled with fragments of calcium chloride. Now open the stopcock *s*, and allow about half the mercury to flow out, while *dry* air enters through the drying tube *c*. Next transfer this dry air to the closed limb by inclining the tube sufficiently. Then bring the mercury in both limbs to the same level by drawing off some through the stopcock. Should the volume of air in the closed limb be less than half the tube full, after levelling, transfer sufficient to make up the desired volume, and level again, but this time by removing the cork and pouring into the open limb sufficient mercury. The cork and tube *c* need not be replaced,

FIG. 41.



We have now a confined mass of dry air in the closed limb. Place over this tube a glass jacket *j*, which is stopped below by the cork *f*, through which the closed limb passes, and the small side tube *m*. Fill up the space between the exterior of the U tube and the jacket with pounded ice. This will soon cool down the air in the tube, and the gas will contract in volume. When no further contraction takes place, again adjust the level of the mercury in the two limbs, and mark off as accurately as possible in the outer tube the position of the mercury in the closed limb. This marks on the tube the volume occupied by the dry air at the temperature of melting ice, *i.e.* at o° C.

Now pour tepid water into the jacket *j*; this will melt the remaining ice, and the water will flow off through the side tube *m*, which is opened or closed at pleasure by the pinchcock or clip *p*, that compresses a piece of india-rubber tubing attached to *m*. When the ice has melted, and the water been drawn off, remove the pinchcock *p*, and connect the tube *h*, by means of vulcanised tubing, with a flask from which a good current of steam can be obtained by rapidly boiling water contained in it; the steam rushes through the jacket and the excess may be allowed to pass off into the air through the tube *m*. As the air n the closed limb becomes heated it expands until it has acquired the temperature of the steam. When it ceases to expand, adjust the level of the mercury as before, and mark on the tube the volume occupied by the dry air at the particular temperature.

Now divide the interval between the two points

marked into 100 equal parts, by transferring the length to cardboard, and plotting off the intervals. With the scale thus obtained, measure the distance from the position occupied by the mercury when the gas was cooled to the temperature of melting ice, to the sealed top of the tube, and it will be found that the end of the tube is reached, as nearly as possible, at 273 DIVISIONS of the scale. This point is termed the *absolute zero*, for it is evident that the contraction of the gas could not go beyond this point, even if it contracted with regularity nearly to its limit. If then we represent the top of the tube as absolute zero, or 00°, the enclosed air at the temperature of melting ice will occupy the position 273°, and that of free steam the position of 373°, on such a scale of absolute temperature; hence the 'law' enunciated by Charles, that *the volume of a given mass of gas, under constant pressure, is directly as its* ABSOLUTE *temperature, i.e.*, as its temperature measured from absolute zero. This is $273+t$, t being the number of degrees above the freezing-point on the scale of the centigrade thermometer.

CHAPTER XI.

EXPERIMENTS WITH OXYGEN AND OZONE.

OXYGEN—*Symbol*, O″=16. 1 *Vol weighs* 16 *c. grs.*[1] *Molecular weight*=32.—We have already proved conclusively that oxygen is not only a constituent of water, and that it forms $\frac{8}{9}$ths of that body by weight, but also that it is present in atmospheric air. Later on, we shall find that it is met with in most of the chemical compounds of which the solid crust of our globe is composed, but in the air alone do we find the element in a free state (*i.e.* not in chemical combination), though mixed with four times its volume of another gas called nitrogen. We do not possess a convenient process for the direct separation of oxygen from air, hence we always prepare it from one or other of its compounds. For example, oxygen can be prepared from water by electrolysis, as already described, Experiment 22,

$$H_2O=2H+O,$$

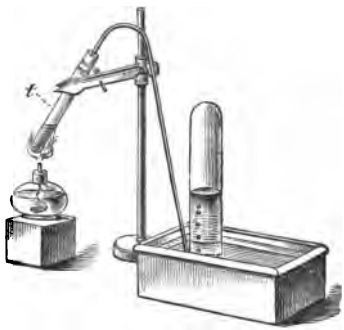
or more conveniently by heating certain bodies which easily yield oxygen—for example—mercuric oxide, or the salt called potassium chlorate.

Experiment 56.—Take a tube of hard glass, *t*, fig. 42, closed at one end, and fitted with a cork and

[1] The actual number is 15·96; but for ordinary purposes of calculation the above value (16) may be used.

delivery tube as shown. Place in the tube about 200 c. grs. of red oxide of mercury, the 'red precipitate' of the druggists. Heat gently at first, and then increase the temperature. Gas will soon escape from the delivery tube and bubble through the water in the pneumatic trough. After expulsion of the air, the gas collected is found to have the property of rekindling a match with a glowing tip, and is oxygen; at the same time it will be observed that bright metallic globules condense on the sides of the tube *t*, and, if the heat be continued long enough, the pure mercuric oxide is wholly resolved into oxygen gas, and globules of the liquid metal mercury or quicksilver. Thus:—

FIG. 42.



$$\underbrace{Hg'' O''}_{\text{Mercuric oxide.}} = \underbrace{Hg}_{\text{Mercury.}} + \underbrace{O}_{\text{Oxygen.}}{}^{1}$$

This process is not an advantageous one for the preparation of oxygen in quantity, but it possesses special interest, since it is the method by which the element was first prepared by its discoverer, Dr. Priestley, in 1774.

Oxygen can also be obtained by heating manga-

[1] Therefore 216 c. grs. of HgO afford 16 c. grs. of O, the weight of one *vol* at 0° C. and 760 mm. See note on last page.

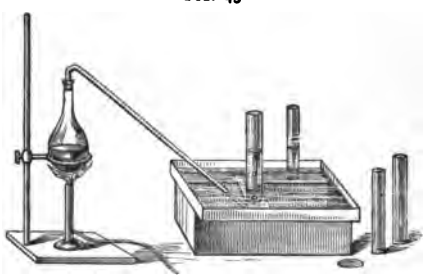
nese dioxide to full redness, in which case the following decomposition takes place—

$$3\ Mn\ O_2 = Mn_3\ O_4 + 2\ O.$$

Barium dioxide and other similar bodies also afford the gas, and the processes will be described under the respective compounds; but the most convenient method is the following :—

Experiment 57.—Fit a flask—a clean Florence oil flask answers well—with a cork and delivery tube

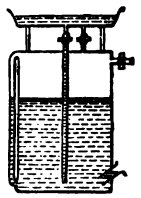
FIG. 43.



as shown in fig. 43. Break up some crystals of the salt potassium chlorate ($KClO_3$) in a mortar, then mix with about one-third of its weight of black oxide of manganese (manganese dioxide or peroxide), and pour the mixture into the flask, but reserve a small portion and heat the latter strongly in a test tube before applying heat to the contents of the flask. If no violent action takes place when the small quantity is heated, the manganese used may be considered free from any dangerous impurity, such as charcoal, soot, or lamp black, with which it is sometimes accidentally mixed

or even adulterated ;[1] then heat the flask. After expulsion of the air, the gas can be collected in several jars or in wide-mouthed bottles over the water in the pneumatic trough, as 100 c.cs. of water dissolve but 2·989 c.cs. of gas at 15° C. If it be desired to store a quantity of the gas for a number of experiments, the gas-holder shown in section, fig. 44, is to be employed.

FIG. 44.



The heat resolves the potassium chlorate into oxygen gas and potassium chloride, which latter remains in the flask at the end of the operation along with the black oxide of manganese ; for the latter body is not known to undergo any chemical change during the operation, though its presence undoubtedly enables the oxygen to separate at a lower temperature than it otherwise would. The following equation represents the ultimate change :—

$$\underbrace{K' Cl' O''_3}_{\text{Potassium chlorate.}} = \underbrace{K' Cl'}_{\text{Potassium chloride.}} + 3O$$

The potassium chloride left is easily soluble in water, whereas the black oxide of manganese is insoluble ; we can take advantage of these facts in order to separate the two bodies. Add some warm water to the contents of the flask, allow the mixture to stand for half an hour or so, and then throw the dirty black mixture on a paper filter. The clear liquid passes

[1] Several fatal accidents have resulted from such admixture.

through and is collected in a beaker, while the solid particles of the insoluble manganese dioxide are retained by the filter and thus separated. When all the liquid has passed through the filter, place the dish on a ring of a retort stand, and evaporate (as in Experiment 50) until all the water is removed, and a white saline body remains. This is the potassium chloride.

With the aid of the equation just given we can easily calculate the weight and the volume of pure oxygen gas, at 0° C. and 760 mm. that a given weight, say 100 c.grs., of the pure potassium chlorate can afford by complete decomposition. The molecular weight of $K Cl O_3$ is 122·6, and this is found by the general method of adding together the weights of the constituent atoms, *i.e.*, K=39·1, Cl=35·5, 3 O=48 (=16×3). Since all the oxygen is evolved when the salt is strongly heated for a sufficient time, it follows that 122·6 c.grs. of $K Cl O_3$ can afford 48 c.grs. of O. Hence the weight of gas 100 c.grs. can yield is—

$$122{\cdot}6 : 100 . \therefore 48 . x \quad (x = 39{\cdot}15 \text{ c.grs. } \textit{Ans.}).$$

We have now to find the volume:—16 c.grs. of oxygen at 0° C. and 760 mm. measure 1 *vol* (=112 c.cs.); now

$$16 : 39{\cdot}15 . \therefore 112 : x \quad (x = 274 \text{ c.cs. } \textit{Ans.}).$$

The general answer therefore is—100 c.grs. of pure potassium chlorate afford 39·15 c.grs. of oxygen gas, which occupies the volume of 274 c.cs. at 0° C. and 760 mm. The same method is employed in all similar calculations, as for instance in the calculation of the

volume of oxygen that can be collected on heating a given weight of red oxide of mercury.[1]

We already know that oxygen gas is colourless, inodorous, and a powerful supporter of combustion. With the jars or bottles of gas already collected make the following experiments :—

Experiment 58.—Take a small lump of charcoal and twist a piece of copper wire round it. Hold the charcoal in the spirit or gas flame until it is kindled, and then plunge it into a jar of oxygen. The charcoal burns energetically in the pure gas, emitting much light and heat. In this and similar experiments it is well to provide a cover for the jar of cardboard, through a hole in which the wire passes. When the combustion is at an end remove the charcoal and pour into the jar some clear *lime water*—note that the latter becomes milky when the mouth of the jar is closed with the hand and the contents shaken. The reason is that the product of the combustion of charcoal (carbon) in oxygen is a gas called carbon dioxide, this forms insoluble *chalk*, or calcium carbonate, when it meets with lime water (solution of calcium hydrate); the latter is, therefore, a *test* for the gas.[2] These reactions are thus represented—

$$\underbrace{C}_{\text{Carbon.}} + 2O = \underbrace{CO_2}_{\text{Carbon dioxide.}}$$

[1] The method is reversed when we desire to calculate the weight of a body required to afford a given volume of gas.

[2] If lime water be shaken in a jar of pure oxygen it does not become turbid.

Then—

$$CO_2 + \underbrace{Ca''(OH)'_2}_{\text{Calcium hydrate.}} = \underbrace{Ca''CO_3}_{\text{Calcium carbonate.}} + H_2O.$$

The chalk is the calcium salt of an acid H_2CO_3 formed by the action of water on the gas CO_2.

Experiment 59.—Place a small quantity of sulphur in the iron spoon, fig. 45, and kindle it, when feebly burning plunge it into a jar of oxygen. The sulphur burns with a beautiful blue flame, and a gas—sulphur dioxide—having a suffocating odour, is the product. Remove the spoon, pour some water into the jar, close the mouth with the hand and shake. Now test the water in the jar with some blue litmus paper. It will be found to *redden* the paper, and to have a sour taste. In the first instance—

FIG. 45.

$$\underbrace{S}_{\text{Sulphur.}} + 2O = \underbrace{SO_2}_{\text{Sulphur dioxide.}}.$$

The sulphur dioxide gas when dissolved in water produces sulphurous acid, thus—

$$\underbrace{SO_2}_{\text{Sulphur dioxide.}} + H_2O = \underbrace{H_2SO_3}_{\text{Sulphurous acid.}}.$$

Experiment 60.—Clean the spoon used in the last experiment and place in it a very small dry piece

of phosphorus.[1] Kindle and plunge into a jar of oxygen. It burns with great brilliancy and produces white fumes in abundance; these deposit as a white powder on the sides of the jar, if the latter be nearly dry. Remove the spoon and pour some cold water into the jar and shake as before. The white substance disappears, dissolving in the water; this solution also is found to contain an acid. The first change is thus expressed—

$$\underbrace{2P^{v}}_{\text{Phosphorus.}} + 5O'' = \underbrace{P^{v}_{2}O''_{5}}_{\text{Phosphorus pentoxide.}}$$

Then—

$$\underbrace{P_2O_5}_{\text{Phosphorous pentoxide.}} + H_2O = \underbrace{2(HPO_3).}_{\text{Metaphosphoric acid}}$$

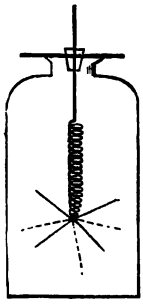
In each of these experiments, then, an *oxide* was the product of combustion in oxygen, and the oxide produced an acid when added to water. The name of the element[2] signifying 'acid producer' was given in allusion to this property, but it is now known to be only one amongst several elements which can give rise to compounds exhibiting acid characters.

Experiment 61.—Take a piece of thin iron wire and coil it into a spiral, twist one end of the spiral round a small splinter of wood coated with sulphur. Now set fire to the latter and plunge the coil into a

[1] Take care to cut this under water, and then dry the fragment to be used by very gentle pressure between folds of blotting paper. Phosphorus is easily ignited by friction, and it burns with great violence. [2] Ὀξύς, acid; γεννάω, I generate.

large jar of oxygen, as shown in fig. 46. The sulphur and the match burn and soon raise the temperature of the iron to such a point that it undergoes strong combustion, molten drops falling from the point of wire into the water covering the bottom of the jar. When the combustion is ended, the jar is removed and the solidified drops examined. They consist of an oxide of iron, but they do not produce an *acid* with water under any conditions, nor do they exhibit any alkaline or basic characters.

FIG. 46.



$$3Fe+4O=Fe_3O_4.$$

Again, when hydrogen burns in air or in oxygen, it produces *water*, which we already know to be a liquid that does not present the ordinary characters of an acid or of a base.

We thus learn that all oxides do not produce acids, though some do; further that some oxides do not produce either acids or bases, and may be classed as *indifferent* oxides.

Experiment 62.—Place a small piece of the metal sodium in the little spoon, shown in fig. 45, heat the metal until it fuses and begins to burn, plunge then into a jar of oxygen. The sodium produces a white or nearly white body (Na_2O) which dissolves in water with a hissing noise and produces a liquid which is strongly *alkaline* to test paper. Thus—

$$\underbrace{2Na'}_{\text{Sodium.}} + O'' = \underbrace{Na'_2O''}_{\substack{\text{Sodium} \\ \text{oxide.}}}.$$

Then—

$$\underbrace{Na_2O}_{\text{Sodium oxide.}} + H_2O = \underbrace{2(NaOH)}_{\text{Sodium hydrate, or caustic soda.}}.$$

A similar experiment can be made with the metal potassium.

Experiment 63.—Finally, burn a piece of magnesium wire or ribbon in air or oxygen, and throw the white solid produced (magnesium oxide, or 'magnesia,') into a small quantity of water.[1] Although the body does not seem to dissolve in the water, the latter acquires an alkaline reaction if allowed to stand for some time, and a piece of reddened litmus paper left in the liquid becomes blue.

$$\underbrace{Mg''}_{\text{Magnesium}} + O'' = \underbrace{Mg''O''}_{\text{Magnesium oxide.}}.$$

Then—

$$\underbrace{Mg''O''}_{\text{Magnesium oxide.}} + H_2O = \underbrace{Mg''(OH)'_2}_{\text{Magnesium hydrate.}}.$$

[1] Similarly a lump of common 'quicklime,' or calcium oxide—CaO—used in the preparation of mortar, when added to water falls to powder and dissolves to a small extent, affording an alkaline solution or 'lime water.' If but a small quantity of water be poured over the lime, it is absorbed and the mass crumbles to a powder consisting of calcium hydrate—$Ca(OH)_2$—much heat resulting from the chemical union of the lime and water. (See further Part III. Experiment 619.)

Our results may be thus tabulated—

Acid producing Oxides—

Carbon dioxide . . .	CO_2.
Sulphur dioxide . . .	SO_2.
Phosphorus pentoxide . .	P_2O_5.

Indifferent Oxides—

Water	H_2O.
Iron oxide	Fe_3O_4.

Basic Oxides—

Sodium oxide	Na_2O.
Potassium oxide . . .	K_2O
Magnesium oxide . . .	MgO.

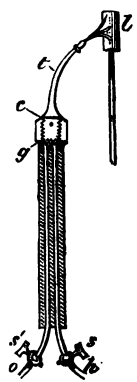
The members of the first class are termed *acid anhydrides*, and those of the third class, *basic anhydrides*[1], because the corresponding acids and bases can yield these oxides directly or indirectly.

Experiment 64.—Fill a stout gas jar with water, and invert in the pneumatic trough in the usual way, introduce oxygen until one-third of the water has been displaced, and then hydrogen until the jar is filled with gas. Slip a glass plate under the mouth of the jar, remove the latter from the trough and apply a flame. A violent explosion takes place, as in the similar Experiment 23, and water is produced, as we have already proved by Experiments 24 and 25, when we exploded the mixture of gases under such conditions that the resulting water could be observed. We shall now make the gaseous mixture burn quietly.

[1] From α and ὕδωρ = without water.

Experiment 65.—Connect the tube *h*, fig. 47, with a small rubber cloth bag full of hydrogen by means of a flexible tube, and *o* with a similar bag containing oxygen gas, the stopcocks *s* and *s'* being closed. Apply *equal* pressure to the bags, and turn on a little hydrogen by cautiously opening the stopcock *s*; the gas passes through the meshes of the wire gauze *g*, placed over the opening of both tubes, and enters the little chamber *c*, whence it passes by the narrow tube *t*, to the jet at which it is to be kindled. While the hydrogen burns, producing a flame 3 or 4 centimeters long, turn on the oxygen gradually by opening *s'*. The flame shortens considerably as the proportion of oxygen increases, up to a certain point, but if too much oxygen be introduced, it is extinguished with a snap, then the stopcocks must be turned off and the same plan of lighting repeated. When burning properly, the *oxyhydrogen* flame is of pale blue colour, and emits little light, but it is intensely hot—in fact the hottest known *flame*.

FIG. 47.



a. Introduce into the flame the end of a piece of platinum wire. The metal melts easily to a globule, though it is almost infusible in our most powerful furnaces.

b. Introduce an iron or steel wire; it also melts quickly, and burns, emitting brilliant sparks.

c. Hold in the flame a piece of quicklime, or one of the cylinders of the same material, commonly sold

for the purpose, *l*, fig. 47. The lime does not melt, but it becomes intensely hot, almost white hot, and emits a brilliant light. This is the oxyhydrogen, or 'limelight,' which is used for various illuminating purposes.

OZONE—*Symbol*, O_3. *Molecular weight*=48.

Experiment 66.—Pour a layer of water on the bottom of a tall and wide-mouthed bottle, and introduce a stick of clean, freshly-scraped phosphorus, taking care that the latter shall not be immersed in the water through more than one-third of its length. Partially close the mouth of the vessel with a piece of card-board, and let it stand for half-an-hour or so. Whitish fumes soon appear, and ultimately fill the bottle: on opening the latter, a strong and peculiar smell is perceived, and when a strip of moist starch and potassium iodide paper [1] is plunged into the air of the bottle, it is quickly discoloured, while pure air is almost without action upon the paper. The peculiar smell and the effect upon the test paper are alike due to the presence of a small quantity of a body discovered by Schönbein in 1840, and named by him *Ozone*.[2]

The strong smell noticed when an electrical machine is worked, or electric sparks are passed through air, is due to the formation of a little ozone; and if the oxygen evolved on the electrolysis of water, as in Experiment 22, be examined with the test-paper, it will also give the colour change just observed. Dr. Andrews, of Belfast, has proved that ozone is nothing

[1] Easily prepared by soaking pieces of white bibulous paper in a mixture of thin starch paste, with aqueous solution of potassium iodide.

[2] Ὄζω, I smell.

but free oxygen in a remarkably active condition, for pure, dry oxygen can be partially converted into ozone by the silent electrical discharge,[1] and the oxygen during conversion is found to *contract* in volume. In fact, it has been shown that three volumes of ordinary oxygen form two volumes of ozone; the molecule of the latter therefore contains *three* atoms (unlike so many other elementary molecules, which contain two); hence, ozone may be correctly spoken of as a chemically condensed and active modification of ordinary oxygen, and its symbol written O_3. On heating ozone to 260° C. it is reconverted into ordinary oxygen, and the gas returns to its original volume, while it loses the power of affecting the test paper.

This remarkable instance of what is termed *allotropism*[2] is not the only example of an element occurring in two forms which differ in physical and chemical characters, and yet consist of the same matter; for we shall meet, later on, with analogous allotropic forms of phosphorus, sulphur, and of carbon—the black and dull charcoal and the colourless and brilliant diamond being but allotropes of the element carbon.

Isomerism[3] in compounds is the condition analogous to allotropism of elements; we are acquainted with pairs of compounds which contain the same elements in the same proportions, but exhibit different

[1] Under the most favourable circumstances the proportion of ozone formed in a given volume of oxygen rarely exceeds one-tenth of the whole, even when a Siemens' or Houzeau's electrical ozoniser is employed.

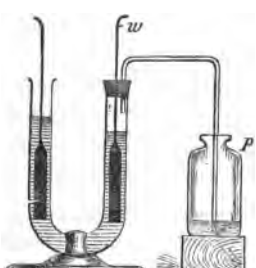
[2] From ἄλλος, another, and τροπος, habit or condition.

[3] From ἴσος, equal, and μέρος, part.

physical and chemical characters; for example, lactic acid, met with in sour milk, and solid grape sugar. But we have in two bodies, whose empirical formula is in each case CON_2H_4, illustrations of a special kind of isomerism. One of these substances, *ammonium cyanate*, is easily converted by heat into the second, a body termed *urea*, and the latter is identical with a well-known product of the animal organism. (See Appendix and Part IV. for details.)

Experiment 67.—Pour a small quantity of perfectly bright clean mercury into a short wide test tube, and lower the latter by means of a string into the jar containing ozone used in the last experiment. Note that a very short exposure to the ozonised air suffices to render the surface of the mercury dull, owing to the production of a film of an oxide of mercury. Pure oxygen does not affect pure mercury under the same conditions, but the more energetic ozone rapidly tarnishes or oxidises the metal. A piece of rubber tubing is also quickly attacked by ozone.

FIG. 48.



Experiment 68.—Bend a tube about 50 centimeters long and 1·5 c.ms. diameter into U form. Fit one opening with a cork carrying the bent gas delivery tube, as shown, fig. 48, and through the cork pass a stout platinum wire terminating within the tube in a strip of foil of the same metal. Before inserting

the cork, coat it (but not the platinum) thoroughly with molten *paraffin*, as the latter is not affected by ozone, and serves to protect the cork from the influence of the gas. Let the end of the small gas delivery tube dip under the surface of a small quantity of *ether* contained in the phial *p*. Now connect the wire *w* with the platinum end of a small two-cell Grove's battery, and insert the other pole in the open limb and *well down into the bend* of the U tube, which latter has been previously half filled with water acidulated with chromic acid, or, if the latter is not available, with sulphuric acid (one volume of strong acid to three of water). Oxygen containing a little ozone will be evolved from the plate *w*, but, having no exit save from the gas delivery tube, will bubble through the ether. The latter dissolves the ozone, and after some time becomes so charged with that body that it instantly discolours the ozone test paper when a strip is dipped into the liquid. Moreover, when some of the ozonised ether is shaken up with water, coloured of a pale blue tint by 'sulphate of indigo,' the colour is destroyed, and the liquid thus bleached. Ozone is also soluble in turpentine and several essential oils, but it is dissolved to a very small extent by water: according to Carius only 0·5 c.c. in 100.

Experiment 69.—Expose a piece of ozone test paper freely to the outer air for a few hours, shading it, however, from sunshine. Even prolonged exposure to the air of a large city rarely produces discolouration of the paper, but pure country air usually causes a distinct brownish colouration in a few minutes. It

has been proved that ozone is present in pure air in minute proportions, though other bodies are occasionally met with which likewise discolour the paper. It is supposed that the blue colour of the 'sky' is due to the presence of ozone.

It is not surprising that city air should contain but little ozone, as the organic and other impurities destroy, and, we may add, at the same time are destroyed by the ozone, which latter, therefore, acts as a natural disinfectant by reason of its extremely energetic oxidising power.

When highly ozonised oxygen or air is inhaled into the lungs, much bronchial irritation results; but a small proportion does not produce any sensible effect.

We have thus studied in some detail the two strongly contrasted and typical elements hydrogen and oxygen. The products of their union now require further examination at our hands, in order that we may complete the first stage of our inquiry.

CHAPTER XII.

EXPERIMENTS WITH WATER AND HYDROGEN PEROXIDE.

OUR previous experiments having placed beyond doubt the composition of water by weight and volume, and its molecular weight ($H_2O=18$), we have now to examine some of the more prominent characters of this most important of all liquids.

Experiment 70.—Arrange the stoppered retort A,

FIG. 49.

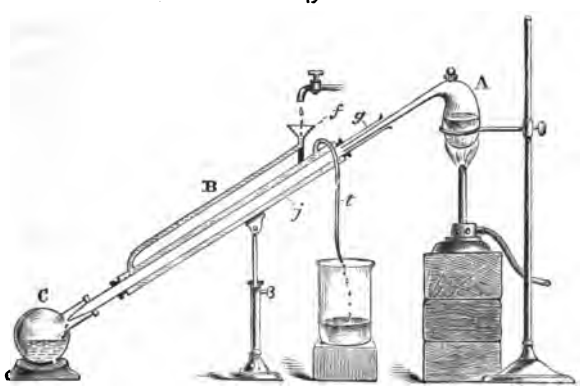


fig. 49, Liebig's condenser, B, and receiver C, as shown. Introduce some rain or river water into A,

using a funnel for the purpose, and apply the heat of a spirit or gas flame, taking care to move the latter about at first and to wipe off drops of moisture that form on the bottom of the retort. When the water has been thus warmed at first, the lamp flame may be allowed to play steadily on the retort. After a short time the water *boils*[1] vigorously, and the steam passes into the beak of the retort, and ultimately into the inner glass tube *g*, of the condenser; here it is cooled and condenses to water, and the latter runs into the receiver. The glass tube, passing water-tight through the tin plate jacket *j*, is cooled by a current of cold water, which enters through the funnel *f* at the lowest point of the apparatus, while the warmer and therefore lighter water, to which the steam has parted with most of its heat, is carried away by the tube *t*, at the upper part of the condenser. The first portions of the condensed steam, or *distilled water*, are to be thrown away and the rest collected in the receiver; but it is not advisable to continue the distillation after the liquid in the retort has been reduced to one-fifth of its original volume. The water thus collected is almost chemically pure.

Water, when thus pure, is a colourless,[2] inodorous, and insipid liquid, which at ordinary temperatures

[1] A liquid is said to boil when the temperature is reached at which the pressure (tension) of its vapour is equal to that of the atmosphere at the time. In the case of water this temperature is 100° C. at 760 mm. The temperature of ebullition depends on the particular liquid heated, and for a given liquid rises and falls with increased or diminished pressure.

[2] Great masses of pure water have a distinct bluish colour.

gives off invisible vapour, and diffuses into the surrounding air ; hence, water can be slowly but wholly evaporated by simple exposure to the air. When heat is applied it can be rapidly and completely converted into steam—one volume of water affording nearly 1,700 volumes of steam at 100° C. and a pressure of 760 mm. One gram of steam at 100° C. passed into ice-cold water can raise the temperature of 537 grams of the latter 1° C. The 'latent heat of steam' is, therefore, 537 thermal units. Water becomes solid when sufficiently cooled, either by its own rapid evaporation, or by the application of external cold.

Experiment 71.—Place a few drops of pure water in a watch-glass and suspend the latter over a basin containing strong oil of vitriol, standing on the plate of an air-pump. Now cover the whole with a small bell jar and exhaust the air. As the pressure diminishes, rapid evaporation of the water takes place, while the vapour is absorbed by the oil of vitriol. The quantity of heat abstracted by rapid conversion into vapour is sufficient to cool the water down to the freezing point in a very short time, and a small piece of ice is quickly produced. Several ingenious ice-making machines have been constructed on this principle.

Experiment 72.—Take a tube about 30 c. ms. long and 4 mm. internal diameter. One end must be closed and expanded into a bulb. Pour in water until the long tube is three-fourths full. Now immerse the bulb and half the stem in a beaker of water ice cold and containing ice. The water in the stem first

rises, owing to the contraction of the glass on cooling, diminishing the capacity of the vessel and pushing up the column of water; as the water cools, however, it contracts more rapidly than the glass, and the level of liquid sinks below the starting point until it becomes stationary and, if the external water be really ice cold, *then rises again in the tube.* If a thermometer could be plunged in the water within the bulb, it would be found to mark about 4° C. when the liquid commenced to rise. Now remove the bulb and plunge it into a 'freezing mixture'[1] of 'Glauber's salt' and common 'muriatic acid,'—the salt just covered with acid. The expansion of the liquid goes on until a sudden check is observed; if the bulb be then removed, it will probably be found cracked and containing ice.[2] Thus water, when cooled down, contracts until the temperature of 4° C. is reached; then it *expands again up to the solidifying point,* and still greater expansion *at* that point suffices to burst the containing vessel, if it offers any obstacle to the free motion of the ice, for the latter occupies, weight for weight, more space than water at 0° C. The temperature of *maximum density* of water is 4° C., or that temperature at which one cubic centimeter of water has the greatest weight, *i.e.*, one gram.

[1] Pounded ice mixed with half its weight of common salt may be used instead, but the mixture given above is convenient and effective.

[2] This sudden expansion on freezing aids materially in the disintegration of rocks, as the water contained in the cavities and fissures, when converted into ice, expands with great force, and breaks up successive layers of the material. The same cause leads to the bursting of water-pipes.

If similar experiments are made with alcohol, oils, and other liquids, they will be found to contract but not to expand again as the temperature is reduced; thus water is a great exception to this general law, and in this respect stands almost alone amongst the liquids hitherto examined.

Unimportant though this property of water may seem to be, its consequences are of great moment to mankind. Thus, if water obeyed the ordinary law, our rivers and lakes would soon become masses of solid ice, their fish would be destroyed, and the heat of summer would be unable to undo the effect of the winter's cold; while the climate would probably be so altered as to render any save equatorial regions almost uninhabitable.

We thus have 'evidence of design' in this exceptional property of water, which exceeds in importance any afforded by the animal or vegetable kingdoms.

When ice at 0°C. melts, it absorbs *without elevation of temperature* as much heat as would raise the temperature of an equal weight of water from 0°C. to 79°C.[1] This quantity of heat is required to change the state from solid to liquid water, and is spoken of as its *latent heat, i.e.*, hidden (insensible) heat.

Experiment 73.—Take three Florence flasks and place in each 100 c. cs. of cold water. Weigh out roughly 50 grams of 'blue vitriol' (crystallised copper sulphate), and introduce into one of the flasks; 50 grams of red potassium bichromate, into another; and 50 grams of common salt into the

[1] Or 79 times its weight of water 1°C.

third. Now boil the contents of each flask: note that the copper and bichromate alike dissolve completely on boiling, each body communicating its colour to the liquid. But even long continued boiling fails to dissolve all the common salt. Therefore common salt is less soluble than the other two bodies in boiling water. As a matter of fact, bodies vary greatly in solubility: some dissolve to such a small extent that they are commonly spoken of as insoluble, for example, chalk and glass; others so freely that they are almost indefinitely soluble, for example, caustic potash and calcium chloride.

When the contents of the three flasks are quite cold, it will be found that beautiful *crystals* have separated in the copper and the bichromate solutions, and these crystals can be made to disappear and reappear by alternate heating and slow cooling of each liquid. It is therefore evident that heat increases the solubility of both solids in water, and that the excess of solid[1] over and above that which the cold liquid can dissolve separates out, thus leaving a solution which cannot dissolve more of the particular body at the given temperature, and is therefore said to be a cold *saturated* solution. A hot saturated solution is obtained by adding the desired substance to boiling water until the solid ceases to dissolve. The

[1] When decomposition does not accompany the act of solution, the crystals which separate from the hot solution have the same composition as the body originally dissolved. If decomposition precedes solution, as when sodium and potassium dissolve in water, Experiments 45 and 46, the body in solution must be different from that introduced.

solubility of a non-volatile solid is usually determined by evaporating a weighed quantity of its solution, saturated at a known temperature, until the solvent is completely expelled; the dry solid residuum is then accurately weighed and the ratio of the solid to the solvent liquid thus directly determined.[1]

Experiment 74.—Pour off into a large test tube some of the cold and clear saturated solution of common salt prepared in the last experiment, now boil, and add a little dry common salt; the latter evidently does not dissolve to any material extent, therefore the solubility of common salt in water is *nearly the same* at high and low temperatures, and in this respect salt is a remarkable exception to the general rule that solids are more soluble in hot than cold liquids.

Experiment 75.—Boil some cold and saturated 'lime water' (see page 117) in a flask, and note that the liquid becomes turbid. This is due to the separation of some of the previously dissolved lime, its solubility in boiling water being little more than half that near to the freezing point. Lime is therefore another exception to the general rule, as it is *less* soluble at high than at low temperature.

Experiment 76.—Take four test tubes and half fill each with water. Add a few drops of alcohol to one, of chloroform to another, of oil to a third, and of glycerine to a fourth. Note that the alcohol and glycerine readily dissolve in, or mix with, the water when the contents of the tubes are shaken up, and

[1] Water saturated with one salt can dissolve others: thus a saturated solution of common salt can still dissolve either copper sulphate or red chromate of potassium.

the water can take up an indefinite quantity of each. On the other hand, agitation fails to make the chloroform or oil disappear, but when the clear water is poured off from the layer of heavy chloroform, it has the odour and sweetish taste of the latter : therefore chloroform is slightly soluble in water. The oil, on the other hand, fails to dissolve to any sensible extent.

Hence water is not equally *miscible* with all liquids.

Experiment 77.—Obtain a bottle of 'soda water.'[1] On removing the pressure of the cork, a rush of *gas* takes place. When effervescence has subsided, pour some of the liquid into a flask and heat : effervescence recurs, and a cork lightly inserted in the mouth of the flask is quickly blown out, owing to the escape of much gas. If the liquid be boiled and then allowed to cool, it will be found to have lost its brisk taste, due to the presence of the gas, for the latter has been wholly *expelled by heat.*

Place another portion in a beaker or tumbler, and the latter on the plate of an air-pump, cover with the bell-jar and exhaust. As the *pressure* within the receiver diminishes, strong effervescence commences in the liquid and continues as the exhaustion proceeds, until all but the most minute traces of gas are removed from the liquid.[2] It is clear, then, that the

[1] The amount of 'soda' present is usually so small that we may regard it as a solution of carbonic acid gas in water.

[2] Although the weight of any gas dissolved does not, generally speaking, diminish regularly with increase of temperature, *the weight dissolved at a constant temperature is directly as the*

gas present in this solution—called 'carbonic acid gas'—is rather freely soluble in water, unlike hydrogen and oxygen,[1] which we have already found to dissolve to an almost insensible extent; and later on (Part II.) we shall meet with much wider differences in solubility; but the fact is that all gases are more or less soluble in water.

Water, then, dissolves solids, liquids, and gases; and all our experience proves it to be the most general solvent known.

Owing to the general solvent power of water, it is not obtainable in an absolutely pure form in nature, since rain derives gaseous and even solid impurities from the air through which it passes, and from the soil on which it falls.

The prime source of all water supply is, undoubtedly, the ocean, since in nature there is a continuous circulation from the sea to the air, then from air to rivers, and, finally, to sea again. The air in contact with the ocean becomes quickly saturated with the vapour of water, and then, being carried by currents over the earth and suddenly cooled, lets fall

pressure, while the volume is the same for all pressures (Henry's Law).

The solubility of gas in water can be determined by agitating together known volumes of gas and water in a graduated tube closed by mercury, and noting the volume absorbed at constant temperature and pressure.

[1] Atmospheric air is soluble to a very small extent in water, 100 c.cs. of the latter dissolving only 1.7 c.cs. of air at mean temperature. Small though this amount seems to be, it is from this source that fish obtain the air necessary for their respiration.

much of the aqueous vapour in the form of rain.[1] If the soil be not very porous, small streams are formed (which wash out soluble impurities from the surface soil), and these flowing into a common channel produce a river. If the soil be porous, the water percolates through it, and may drain away again at a lower level and form rivulets and rivers, or it sinks into the subjacent permeable strata, thus serving to maintain the supply of wells and of natural springs, often situated at a great distance from the place of rainfall. If the permeable strata are not overlaid by those only slightly pervious, land-springs not rising above the surface are obtained over the district; but if the strata dip between two impermeable beds, an Artesian spring is obtained on boring, at a lower level, through the upper bed to the water-bearing strata. Water in its passage through the rock strata, often under considerable pressure, dissolves out more or less of the soluble constituents of the strata, and makes its appearance in land-springs and natural or artificial Artesian wells or springs as a *mineralised* water. If the rocks, through whose substance or fissures it passes in its downward course to find its level, happen to be the older metamorphic, granitic, or quartzose rocks, or green-sand beds, but little impurity is taken up, and the springs usually yield a supply of very pure water. If the rocks are cretaceous, or magnesian, or both, the water is then charged with lime and other salts, to an extent dependent on the particular

[1] If the rainfall of a district be known, the calculations for the catchment area can be easily made, if it be remembered that a fall of 10 inches of rain yields 226,170 gallons per acre.

salts present in the beds, and on their solubility.[1] Water filtering through a bed of chalk dissolves but little of the latter, if the liquid be not charged with carbonic acid, since the amount of chalk (calcium carbonate) taken up bears a direct relation to the quantity of this dissolved carbonic acid. Sometimes, as in the case of the Carara springs, the water becomes charged, probably under pressure, to an unusual extent with acid and with chalk, and on issuing from the source loses much of its carbonic acid; the result of this loss is the deposition of the chalk, previously held in solution by the acid, in stalactitic forms on any objects with which the liquid comes in contact.

If, instead of passing through strata containing lime, magnesian, or alkaline salts, the water charged with carbonic acid comes in contact with decomposable ferruginous rocks, the latter yield up a portion of their iron as ferrous carbonate, which dissolves in the excess of carbonic acid, and forms the water of a chalybeate spa. These spas we often meet with in volcanic districts, and also in the neighbourhood of the coal measures. In the latter localities we rarely fail to meet not only with springs, more or less worthy of the name chalybeate, but we also find

[1] Water rich in calcium (lime) salts is 'hard'—that is to say, it destroys much soap before a lather is produced. The 'hardness,' due to the presence of calcium (and magnesium) carbonate dissolved by carbonic acid, is removed by boiling the water, and is called 'temporary hardness;' that not removed by boiling is 'permanent hardness,' and is due to dissolved chloride or sulphate of calcium or of magnesium. See further, Part III., Calcium, and Part IV., Soap.

the sulphur spas, the sulphuretted compounds of which have been chiefly derived from the decomposition of sulphides, always present in the shales and true coal beds, by infiltrating water charged with carbonic acid.

The most celebrated of these mineralised waters of medicinal value may be thus grouped, according to their chief constituents :—

Carbonated and Alkaline, as those of Vichy, Bilin, Ems, and Malvern.

Sulphated (Sodium), Carlsbad, Cheltenham, Püllna (Magnesium), Epsom, Sedlitz.

Sulphuretted, Harrogate, Aix-la-Chapelle, Lucan, Lisdoonvarna.

Chlorinated, Leamington, Harrogate, Cheltenham, Wiesbaden, Homburg, Kissingen.

Chalybeate, Spa, Tunbridge, Harrogate, &c.

In addition to these, we meet with special products of the action of volcanic gases and steam in the—

Siliceous waters of the Icelandic Geysers.

Boracic waters of the Tuscan lagoons.

Sea water is the product of continual land washing, and in it enormous quantities of saline matter are stored.[1] An analysis of the water of the Irish Channel, made by Messrs. Thorpe and Moreton, afforded the following results :—

[1] Sea water is easily rendered potable by Dr. Normandy's process for providing pure water for ships at sea. Salt water is distilled, as in Experiment 70, but in large iron retorts (or *stills*), the salts are left in the retort, and the condensed and pure water, which is flat and insipid at first, is rendered brisk and agreeable by forcing it to dissolve some atmospheric air in a special apparatus.

1000 parts gave—

Sodium chloride	26.439
Potassium „	0.746
Magnesium chloride	3.150
„ bromide	0.070
„ sulphate	2.066
„ nitrate	0.002
Calcium sulphate	1.331
„ carbonate	0.047
Lithium chloride	traces
Ammonium „	„
Iron carbonate	0.005
Silica	traces
Water	966.144

The specific gravity (or relative weights of equal volumes) of the water was 1024.8, if pure water = 1000.

The proportion of saline matter in the water of the Dead Sea is so large that the specific gravity of a recent sample proved to be 1174. (water = 1000). As the specific gravity of the human body, containing as little air as possible, is rarely higher than 1100, it follows that an average man would be buoyed up by the water of the Dead Sea, and could not sink wholly beneath its surface without some effort.

PEROXIDE OF HYDROGEN (Oxygenated Water)—*Symbol*, H_2O_2. *Mol. Weight* = 34.

Experiment 78.—Add, with frequent agitation, about 5 grams of barium peroxide (BaO_2) in powder to 30 c. cs. of diluted sulphuric acid containing 1 c. c. of strong acid; filter, and add some ether to a portion of the filtered liquid and a few

drops of solution of red potassium bichromate, and shake. Note that the ether (which is but little miscible with water) rises coloured of a magnificent blue tint, which is evanescent.

Barium peroxide and sulphuric acid afford hydrogen peroxide (or oxygenated water) and barium sulphate. The latter body being insoluble is filtered off.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

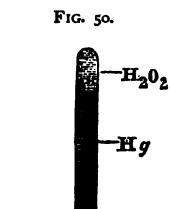
The chromic compound serves to detect the presence of the peroxide of hydrogen formed in this reaction,[1] as it is characteristic of that body to produce an unstable and highly oxidised blue chromic compound which is soluble in ether, and less quickly changes in that liquid than in any other. The solution of H_2O_2 made as above is dilute; when carefully prepared in the first instance, and then evaporated over oil of vitriol in the exhausted receiver of the air pump, a syrupy liquid of specific gravity 1452 (water = 1000) is obtained, which is colourless and inodorous, but has a strong somewhat metallic taste, and can be cooled down to —30°C. without freezing. This is the pure peroxide, but so unstable is it that a slight heat suffices for its decomposition into water and oxygen, and even the dilute solutions of the body sold are easily decomposed in the same way.

Experiment 79.—Take a long and moderately

[1] The peroxide, like ozone, sets free iodine from potassium iodide, and therefore colours the ozone test paper. This colouration by the peroxide takes place even in presence of 'green vitriol' or ferrous sulphate, unlike that due to ozone.

thin glass tube, sealed at one end, three-fourths fill it with mercury, and the remainder with *as strong* [1] a solution of the peroxide as can be obtained: then invert in mercury, as shown, fig. 50. If the tube be inclined, and the portion occupied by the peroxide gently heated by means of a spirit or gas flame, bubbles of gas will quickly make their appearance. When sufficient gas has been collected, pass the thumb under the mercury, close the mouth of the tube, remove from the mercury, invert, and test for oxygen, by plunging a match with a glowing tip into the gas.

FIG. 50.



$$H_2O_2 = H_2O + O.$$

This decomposition of peroxide of hydrogen into water and oxygen gas, can be determined without the aid of heat by mere contact with—

a. Bodies which do not themselves suffer change and are therefore said to act *catalytically*,[2] for example —gold, silver, platinum, charcoal and fibrin of blood.

b. Bodies which lose oxygen at the same time as the peroxide, for example, silver oxide, and peroxide of manganese—the latter especially in presence of acid.

[1] If the solution be very dilute, little gas will be obtained. Any free acid present should be just neutralised by a few drops of caustic soda.

[2] The unmeaning term, *catalysis*, is sometimes applied to cases similar to the above, where we are at present unable to give a substantial explanation of the *modus operandi* of a body that brings about chemical changes in adjacent matter, without itself suffering sensible alteration.

Experiment 80.—Moisten a sheet of writing paper with a solution of lead acetate, and expose it to the fumes arising from a few drops of *ammonium sulphide* sprinkled over the bottom of a shallow dish. The paper becomes quickly discoloured, owing to the production of the dark-coloured lead sulphide (PbS). When stained a dark brown, remove the paper and dry it, then charge a brush with a solution of peroxide of hydrogen, and draw a design on the stained surface. The dark lead sulphide will be rapidly *bleached* by the peroxide, and the design will appear in white on a dark ground. In this case, the peroxide acts as a powerful *oxidising* agent, converting the dark lead sulp*hide* into white lead sulp*hate*, ($PbSO_4$), thus—

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$

In a similar way, discoloured oil paintings and engravings can be bleached by careful treatment with dilute solutions of the peroxide. The latter has also been largely used to bleach dark hair, and change it to the golden colour, lately fashionable.

The chromic test, described under Experiment 78, is another example of oxidation effected by the peroxide, but in that case colour is developed, not destroyed.[1]

[1] Another case of oxidation by the peroxide accompanied by a colour change is the following:—Add a few drops of a fresh alcoholic solution of guiacum resin to a few c.cs. of water, then a few drops of solution of the peroxide to the turbid liquid. If to the mixture a little colouring matter of *blood* be added, a beautiful turquoise blue tint is soon developed. In this case the blood determines the decomposition of the peroxide whose

Although the peroxide cannot be converted into gas, and have its specific gravity taken in that condition so as to determine its molecular weight, its analysis, and the reactions already cited, leave no doubt that its formula is H_2O_2. Its relation to water may be thus shown—

Water.	Peroxide.
H—O—H	H—O—⋮—O—H.

In the peroxide we assume that the two double-link oxygen atoms are united, and form a chain, to each end of which is attached a single-link hydrogen atom. If we break this chain at the dotted line, it is evident that we get two groups, each containing one atom of oxygen and of hydrogen, and each group is expressed by the symbol OH. We should not expect, and do not find, these groups to exist in the free state, because each would have one link of oxygen free, and that is contrary to the general rule ; but we might look for OH in combination. As a matter of fact we meet with the group OH in an immense variety of oxygenated compounds, and this group acts like a single atom of a monad or uni-link element, and is commonly spoken of as the 'compound radicle,' *hydroxyl.* The molecule of the peroxide of hydrogen contains two hydroxyl groups, and therefore is to be regarded as the free molecule of that body.

The study of water and peroxide of hydrogen —two distinct compounds of the same elements—leads

atom of available oxygen at once oxidises the finely divided resin into the blue coloured body. This is Dr. Day's, of Geelong, test for blood.

to the conclusion that, '*when two or more compounds of the same elements exist, combination takes place between them in proportions which are strictly multiples of the respective atomic weights.*' This is Dalton's 'Law of Multiple Proportions,' and is an obvious consequence of the atomic theory.

APPENDIX.

ALL cases of true chemical change met with in chemistry may be referred to one or other of the following divisions. As one or more examples of each kind of change occur in the foregoing experiments, the reader is advised to refer each case he has met with to its proper division. In order to facilitate this process of generalisation, a single example, with its reference, is given under each head.

1. *Cases of direct combination of elements.*

(EXPERIMENT 2.)

$$\underset{\text{Magnesium.}}{Mg} + \underset{\text{Oxygen.}}{O} = \underset{\text{Magnesium oxide.}}{MgO}$$

2. *Cases of simple decomposition.*

(EXPERIMENT 22.)

$$\underset{\text{Water.}}{H_2O} = \underset{\text{Hydrogen.}}{2H} + \underset{\text{Oxygen.}}{O}$$

3. *Cases of double decomposition.*

(EXPERIMENT 14.)

$$\underset{\text{Silver nitrate.}}{AgNO_3} + \underset{\text{Sodium chloride (common salt).}}{NaCl} = \underset{\text{Silver chloride.}}{AgCl} + \underset{\text{Sodium nitrate.}}{NaNO_3}$$

4. *Cases of decomposition by substitution.*

(EXPERIMENT 19.)

$$\underset{\text{Zinc.}}{Zn} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + \underset{\text{Hydrogen.}}{2H}$$

5. *Cases of decomposition by reduction.*

(EXPERIMENT 52).

$$\underset{\text{Copper oxide.}}{CuO} + \underset{\text{Hydrogen.}}{2H} = \underset{\text{Copper.}}{Cu} + \underset{\text{Water.}}{H_2O}$$

6. *Cases of rearrangement, or isomeric change.*

(PAGE 122.)

$$\underset{\text{Ammonium cyanate.}}{NH_4CNO} = \underset{\text{Urea.}}{CO(NH_2)_2}$$

BERTHOLLET'S LAWS.

Two conditions tend so materially to determine double decomposition that Berthollet has enunciated the following 'laws':—

1. Two bodies in solution will always decompose each other, if it be possible, by double decomposition, to produce a new body *less soluble* than either of the two original substances.

For example—silver nitrate and common salt produce insoluble silver chloride. (Experiment 14.)

2. Two bodies when mixed or heated together will always decompose each other, if it be possible, by double decomposition, to produce a new body *more volatile* than either of the two original substances.

For example—'bread soda' or sodium hydrogen carbonate and hydrochloric acid produce the gas carbon dioxide at ordinary temperatures. (Experiment 42.)

Exceptions to these rules exist, but these will be noticed in their proper places.

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INDEX TO PART I.

ABS

ABSOLUTE zero, 105
Acid anhydrides, 118
Acid producing oxides, 118
Acid radical, definition of, 85
Acid salt, 84
Acids, tests for, 80
Agents determining chemical action, 3
Alkalies, 81
Allotropism, 121
Ampère's law, 48
Analysis, 8
Analysis, qualitative, 69
Artiads, 76
Aspirator, 34
Atom, definition, 53
Atometer, 58
Atomic heat, 57
Atomic theory, 53
Atomic weight, definition, 52
Atomic weights, table of, 64
Atomicity or quantivalence, 74
Avogadro's law, 48

BALANCE, 13
Bases, 81, 85
Basic anhydrides, 118
Basic oxides, 118
Berthollet's laws, 144
Binary compounds, 75
Blood, Day's test for, 141
Boyle's law, 101
'Bread Soda,' 5

CANNIZZARO's law 58
Carbon bisulphide. 10
Carbon dioxide, 113
Carbon and sulphur, 10
Caustic potash, 81
Caustic soda, 81
Cavendish eudiometer, 40
Change, physical and chemical, 2

ELE

Charles, law of, 107
Chemical action, determining causes of, 3
Chemical calculations, 103
Chemical equations, 78
Chemical harmonicum, 31
Chemistry, laws of, 15, 19
Combustion of candle in air, 42
Combustion of hydrogen in air, 32
Combustion of magnesium in air, 2
Compounds and elements, 8
Compounds and mixtures, 8
Compound radical, 85, 141
Contraction and expansion of gases, 46
Copper, specific heat of, 57
Crith, 104
Crystallisation, 130

DALTON'S atomic theory, 53
Dalton's law of multiple proportion, 142
Day's test for blood, 140
Definite proportions, law of, 15, 19
Diads, 74
Dibasic acids, 85
Double decomposition, 144
Double salt, 84
Dulong and Petit's law, 58

ELECTRICITY, agent in chemical change, 3
Electricity produced by chemical action, 6
Electrolysis, 35
Electro-positive and electro-negative elements, 69
Electrotyping, 4
Elements, atomicities of, 74
Elements, table of most important, 64
Elements and compounds, 8

EMP

Empirical formulæ, 72
Equations, chemical, 78
Equivalents, 26, 53
Eudiometer, 39

'Fer réduit,' 94
Ferrum redactum, 94
First law of chemistry, 15
Formula, means of finding, 69, 71
Freezing mixture, 128

Harmonicum, chemical, 31
Heat, agent in chemical change, 3, 8
Heat-capacity, 57
Henry's law, 132
Hexads, 74
Hydrates, metallic, 87
Hydrochloric acid, 80
Hydrogen, 21, 28, 45, 86, 90
Hydrogen, absorption of, by metals, 94
Hydrogen as reducing agent, 92
Hydrogen as unit of volume, 102
Hydrogen as unit of weight, 26
Hydrogen, atomic weight of, 52, 64
Hydrogen, combustion of, in air, 32
Hydrogen condensed to liquid, 94
Hydrogen, volume of one c.gr. of, 95
Hydrogen peroxide, 91, 137
Hydrogen and oxygen, 35
Hydroxyl, 141

Indifferent oxides, 118
Isomerism, 121

Latency of bonds, 75
Latent heat of steam, 127, 129
Law of Ampère, 48
Law of Avogadro, 48
Law of Boyle and Mariotte, 101
Law of Cannizzaro, 58
Law of Charles, 107
Law of definite proportion, 19
Law of Dulong and Petit, 58
Law of Henry, 132
Law of multiple proportion, 142
Laws of Berthollet, 144
Laws of chemistry, 15, 19
'Lead tree,' 98
Light, agent in chemical change, 3
Litmus, 80

RAT

Magnesium, 2, 23
Magnesium, heat capacity of, 58, 61
Magnesium oxide, 42, 117
Mariotte's law, 101
Mechanical force, agent in chemical change, 3
Metallic hydrate, 87
Metallic oxide, 89
Metals, electro-chemical series, 66
Metals and non-metals, 65
Mineral waters, varieties of, 136
Modes of chemical change, 144
Molecular weight, 71
Molecule, 52, 53
Monads, 74
Monobasic acids, 85
Multiple proportions, Dalton's law of, 142
Muriatic acid, 80

Nitric acid, 81
Non-metals and metals, 65
Normal salt, 84
Normandy's process, 136

Oxygen, 32, 45
Oxygen, atomic weight of, 52, 64
Oxygen, preparation of, 108, 110
'Oxygenated water,' 91, 137
Oxyhydrogen flame, 119
Ozone, 120
Ozone, tests for, 123

Palladium, absorption of hydrogen by, 94
Perissads, 76
Peroxide of hydrogen, 137
Phosphorus pentoxide, 115
Physical change, 2
Physical constitution of gases, 45
Potassium hydrate, 81
Pressure, correction of gases for, 100
Proportion, law of definite, 15
Proportion, law of multiple, 142
Pyrophoric iron, 92

Qualitative analysis, 69
Quantitative analysis, 69
Quantivalence, or atomicity, 74

Radicals, acid, simple and compound, 85
Rational formulæ, 72

SAL

SALT, 16, 70, 82
Salts, acid and normal, 84
Saturated solution, 130
Sea water, 137
Second law of chemistry, 19
Silver, specific heat of, 57
Silver nitrate, effect of heat on, 13
Silver nitrate and magnesium, 16
Simple radical, 85
Soda-water, 132
Sodium bicarbonate, 5
Sodium chloride, 70, 82
Sodium oxide, 117
Solubility of gases, 132
Solubility of solids, 131
Solvent power of water, 133
Specific gravity of copper and silver, 57
Specific gravity of gases, 45
Sulphide of iron, 10
Sulphur dioxide, 114
Sulphuric acid, 80
Sulphurous acid, 114
Symbols, 63
Symbols of principal elements, 64
Synthesis, 8

TABLE of atomic weights, 64
Temperature, absolute, 105
Temperature, correction of gases for, 101

ZIN

Tension of aqueous vapour, correction for, 100
Tensions, table of, 100
Tetrads, 74
Triads, 74

UNIT of volume, 102
Unit of weight, 26

VOL, definition of, 102
Volume of one c.gr. of hydrogen, 95

WATER, composition by volume, 37, 40
Water, composition by weight, 93
Water, distilled, 126
Water, formula of, 71
Water, frozen by rapid evaporation, 127
Water, latent heat of, 129
Water, maximum density of, 123
Water, mineral, 135
Water, solvent power of, 133
Water, synthesis of, 31, 36, 50

ZERO, absolute, 105
Zinc sulphate, 90

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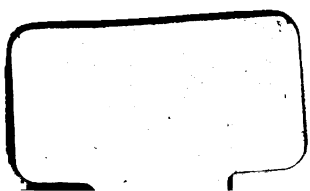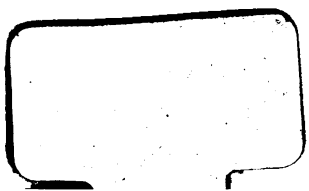
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